HEAT

BY

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SECOND EDITION

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PREFACE

Since the first publication of this textbook, especially noteworthy advances have been made in certain particular phases of the extensive subject of heat. Perhaps the most striking progress has been reported in the field of extremely low temperatures, where the physical properties of materials have been investigated close to the absolute zero. The phenomenal development of nuclear physics in recent years has been greatly aided by knowledge obtained in thermal experiments. This field in turn now offers a challenge to those who would make use of the vast stores of nuclear energy known to be available. In the field of temperature measurement the International Temperature Scale has been generally adopted and many industrial processes are completely dependent upon accurate thermal control.

In so far as possible, references to the recent work is included in this revision. At the same time an effort has been made to make the text adaptable to students with less preparation by including somewhat more descriptive matter and by setting off in smaller type certain more difficult topics which may be omitted with no loss in continuity.

I wish to express appreciation to the many readers who have so kindly taken the trouble to send comments on the text. In carrying out this revision, all suggestions received have been given careful consideration.

The following recently published texts may well be added to the list mentioned at the end of the preface to the first edition: E. F. Burton, H. G. Smith, and J. O. Wilhelm, *Phenomena at the Temperature of Liquid Helium;* M. W. Zemansky, *Heat and Thermodynamics;* R. L. Weber, *Temperature Measurement and Control;* H. S. Allen and R. S. Maxwell, *A Textbook of Heat;* and the monumental volume on *Temperature,* 1941, edited by the American Institute of Physics.

J. M. Cork

September, 1942.

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CHAPTER I

TEMPERATURE AND ITS MEASUREMENT

Temperature. A logical system of physical concepts may be developed on the assumption of the existence of the three fundamental quantities of mechanics, namely, mass, length, and time. To describe those phenomena in which the existence or transfer of heat plays a part, it is necessary to introduce an additional fundamental concept. Historically the thermal quantity that has been recognized as fundamental is temperature. Since our knowledge of the properties of matter can be gained only through sense perception, every fundamental quantity must be ultimately defined in terms of received sensations. The temperature of a body may thus be qualitatively defined as the property of the body that determines the sensation of warmth or coldness received from contact with it. Experience shows that the sense organs are not sufficiently developed to make absolute measurements of temperature. It is a well-known fact that the same body may be described as either warm or cold, depending upon the temperature of the body with which it is compared. It is therefore necessary to adopt arbitrarily by agreement some device for expressing temperatures quantitatively.

Heat and Temperature. Early Greek philosophers proposed various hypotheses to account for heat and fire which along with air, water, and earth made the four primitive substances of the universe. Just as electric phenomena may be explained by assuming either a one-fluid or a two-fluid theory, so thermal phenomena have been explained even well into the nineteenth century. On the one-fluid theory, heat was regarded as a weightless fluid called " caloric," whose abundance or scarcity in a body determined its thermal state. According to the two-fluid theory, the state of a body was determined by the relative amounts of the cold fluid " frigoric " and the hot fluid " caloric," present in the body.

Until the eighteenth century no distinction was made between heat and temperature. Joseph Black (1728–1799) was perhaps the first to write on this subject. Although believing in the one-fluid caloric theory, he pointed out that one must distinguish between the quantity and the intensity of heat, the former depending on the amount of caloric present and the latter on the temperature. The modern notion that heat is simply the energy of random motion associated with the particles of which a substance is composed was not generally accepted until about the middle of the nineteenth century.

Regardless of what theory was held concerning the nature of heat a universally acceptable definition could be made, following the definition of temperature. Thus heat is that something which if present in a body in larger quantity results in a more acute sensation of warmth being received from the body, provided that no change occurs in its state. Observation of the body reveals the fact that as this change in temperature is taking place there is simultaneously a change in all the other physical properties of the body. Among these changes, the following are worthy of mention:

a. Change in volume.
b. Change in pressure, volume constant.
c. Change in electrical resistance.
d. Change in contact emf.
e. Change in radiation from the surface.
f. Change in state, etc.

The changes in these various physical properties are for the most part susceptible to accurate measurement. It is then possible by agreement to let the change in any particular property serve as a measure of the change in temperature. Each of the above mentioned properties has at some time been employed as the basis of a thermometric scale. It is not to be expected that a temperature measured by an apparatus based upon the change in a particular physical property would agree exactly with the result obtained when using a device based upon a different physical property. Only on that scale adopted by universal agreement would the measured temperatures be correct.

A thermometric scale independent of the particular properties of any substance was proposed in 1848 by Sir William Thomson (Lord Kelvin).[1] This scale was based upon the expression obtained for the efficiency of a reversible engine working between two temperatures and is discussed later on page 234. In the International Temperature Scale adopted in 1933, all temperatures by whatever device measured, should be corrected and expressed in terms of the thermodynamic or Kelvin scale.

Early Fluid Thermometers. The earliest devices used to indicate temperature were known as thermoscopes. They usually consisted of a glass bulb whose volume was several cubic centimeters, filled with air and provided with a long tube extending downward into a vessel containing colored water or other liquid. A scale was attached to the vertical tube and the position of the top of the colored liquid in the stem after a little air had been expelled from the bulb, served to indicate the temperature. The position of the separating surface in the stem of the thermoscope would also depend upon the atmospheric pressure. Figure 1 illustrates a device of this sort.

---

[1] W. Thomson, *Camb. Phil. Soc. Proc.*, **1**, 66 (1848); *Phil. Mag.*, **33**, 313 (1848).

It is quite uncertain who first used the thermoscope to measure temperature. Its invention has been variously ascribed to Galileo Galilei (1561–1612) of Florence in 1593; to C. Drebbel of Alkmaer in Holland in 1609; to Paolo Sarpi (1552–1623) of Venice in 1610; to Sancttario Santario (Sanctorius) (1561–1636) of Padua in 1611; and to G. della Porta (1543–1615) of Naples about 1610. In his great work entitled *Novum Organum*, published in 1620 and written during the preceding decade, Francis Bacon (1561–1626) describes[2] several experiments in which thermoscopes are employed. On this account the invention of the device has often been incorrectly attributed to Bacon himself.

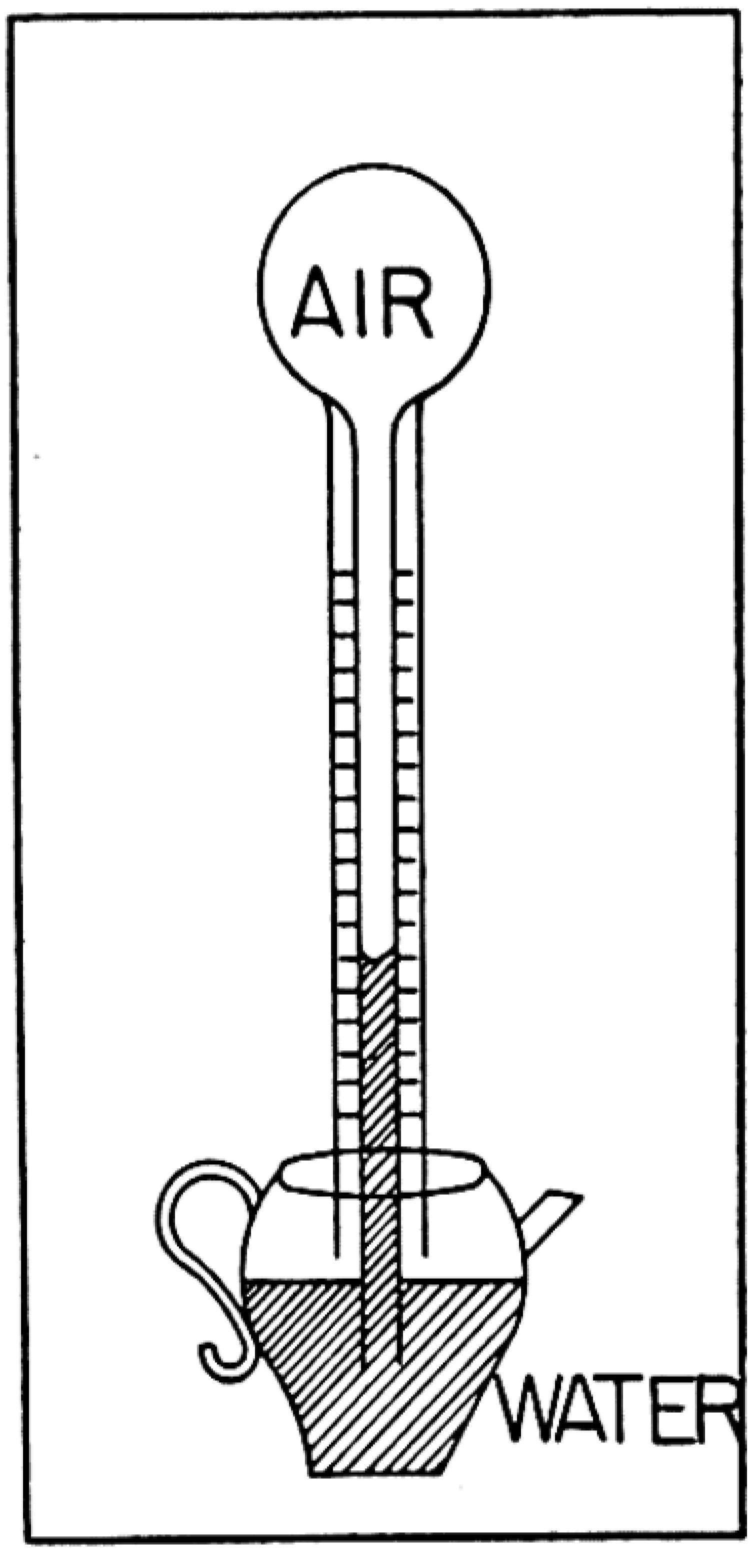

FIG. 1. Florentine thermoscope.

From the thermoscope or air bulb was developed the thermometer in which the bulb was filled with liquid. Galileo is supposed to have used open bulbs filled with wine, and a French doctor, Jean Rey, suggested the use of bulbs filled with colored water about 1632. Sealed thermometers whose readings were consequently independent of changes in atmospheric pressure were made for Ferdinand II, Grand Duke of Tuscany, about 1650. Experiments performed with such devices were described by Lorenzo Magalotti, Secretary of the "Academia del Cimento" in 1667.

Gabriel Fahrenheit (1686–1736) of Danzig and Amsterdam is generally given credit for being the first to use mercury in thermometer bulbs. In *Novum Organum*, Bacon mentions that next to air and water "quicksilver is most sensitive to heat and cold." The thermometers used by Newton in England and the early thermometers of Fahrenheit were described as employing oil or alcohol colored with saffron for the expanding fluid. In 1724, however, Fahrenheit described[3] for the first time a mercury thermometer. The physical properties of mercury make it a satisfactory thermometric fluid. Its coefficient of volumetric expansion is large and fairly uniform. It is usable over a wide range in temperature and does not wet or adhere to the glass. It is only slightly compressible and has a high reflectivity so that it may be readily observed in transparent containers.

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[2] Bacon refers to the thermoscope as "vitrum graduum sive calendare." The adjective *calendare* is not recognized in Latin dictionaries but was undoubtedly used to indicate that the scale was in a vertical column as was the custom in arranging the days in the calendar of that time.

Temperature Scales. The early Florentine thermoscopes had attached scales devised by the various glass workers according to the fancy of the individual. They were thus entirely lacking in uniformity. The importance of selecting certain fixed points and dividing the included interval into a definite number of equal steps was apparently not realized until early in the eighteenth century.

The Römer Scale. Perhaps one of the first thermometric scales based upon fixed points was that devised about 1702 by a Danish astronomer, Professor Ole Römer (1644–1710) of Copenhagen. This scale is described in a volume of collected papers entitled "Adversaria."[4] The calibration of the scale was described as follows: "When the thermometer is completed, filled, and closed, fix by means of snow or crushed ice the point of division 7½, then by means of boiling [water] the point 60." The numbers assigned to these fixed temperatures were associated with a zero which was the temperature of a mixture of ice and salt and was referred to as the "point of artificial freezing." A record of the daily temperatures of the air at Copenhagen for the years 1708–1709 taken with this device is included in "Adversaria."

The Fahrenheit Scale. The early thermometers of Fahrenheit had the same numeration as that used by Römer. On this scale the temperature of the normal human body was expressed as 22½. In a letter written to Professor Hermann Boerhaave, physician and professor of chemistry and botany at the University of Leyden, Fahrenheit complained of the "inelegance" of the scale of Römer with its fractions. It appears that he first used an alteration of the Römer scale in which the numbers were multiplied by four, giving 30 at the ice point and 90 for the body temperature. Later, recognizing the superiority of 96

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[3] D. G. Fahrenheit, *Phil. Trans.* (*London*), **33**, 1 (1724).

[4] Translated and discussed by Kirstine Meyer, Doctoral Dissertation, Copenhagen, 1909; see also *Nature*, **82**, 296 (1910); 139, 395, 585 (1937).

(a number divisible by 12) over 90, a corresponding change was made in expressing the temperature of the body. He thus describes[5] the calibration of his thermometer in 1724: "placing the thermometer in a mixture of sal ammoniac or sea salt, ice, and water a point on the scale will be found which is denoted as zero. A second point is obtained if the same mixture is used without the salt. Denote this position as 30. A third point, designated as 96, is obtained if the thermometer is placed in the mouth so as to acquire the heat of a healthy man."

Fahrenheit remarked on the success that Amontonius had had with the boiling point of water as a fixed temperature, and when he tried this with his thermometer he found the temperature to be 212. He then investigated the boiling points of many other substances, including mercury itself. Realizing that the boiling point of water was affected by the pressure, he described[6] a thermometer to be used for indicating the barometric pressure directly, when placed in boiling water. In subsequent investigations the boiling point of water was kept as 212 and the freezing point chosen as the other fixed point. The temperature of this was adjusted from 30 to 32 degrees, so that the interval between the two points could be represented by the more rational number 180.

The Scale of Réaumur. A thermometric scale that is still in common use in certain European countries was devised in 1731 by R. A. F. de Réaumur (1683–1757), a French physicist. It is commonly supposed that this scale followed from the fact that the particular mixture of alcohol and water used, expanded 80 parts in 1,000 as its temperature was raised from the freezing point to the boiling point of pure water. The first numbers assigned were 1,000° at the freezing point and 1,080° at the boiling point. In later thermometers, mercury was substituted for alcohol and the scale adjusted for zero and 80° at the freezing and boiling points of water, respectively.

The Centigrade Scale. The modern centigrade scale for expressing temperatures may have first been used by Carolus Linnaeus (1707–1778), professor of physics, astronomy, and botany at the University of Upsula. In a report[7] to the Senate of the University in 1745, he described the thermometers he had been using and claimed priority in the use of a scale in which the freezing point of water was designated as zero and the boiling point of water as 100°. It is not certain that other Swedish scientists did not antedate Linnaeus in the use of this scale. It is known that A. Celsius (1701–1744), professor of astronomy and director of the observatory at Upsala carried out many investigations with thermometers but used a scale on which the freezing point of water was indicated as 100° and the boiling point as zero. It is now assumed that, because of the presence of the letter C (for centigrade) always present on the scale, Celsius has been erroneously credited with the invention of the modern centigrade scale. Figure 2 illustrates these various scales of temperature, with the values at the fixed temperatures.

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[5] D. G. Fahrenheit, *Phil. Trans.* (*London*), **33**, 78 (1724).

[6] D. G. Fahrenheit, *Phil. Trans.* (*London*), **33**, 179 (1724).

[7] N. V. Nordenmark, *Svenska Linné-Sällskap Årsskrift*, **18**, 124 (1935); see *Nature*, **136**, 365 (1935).

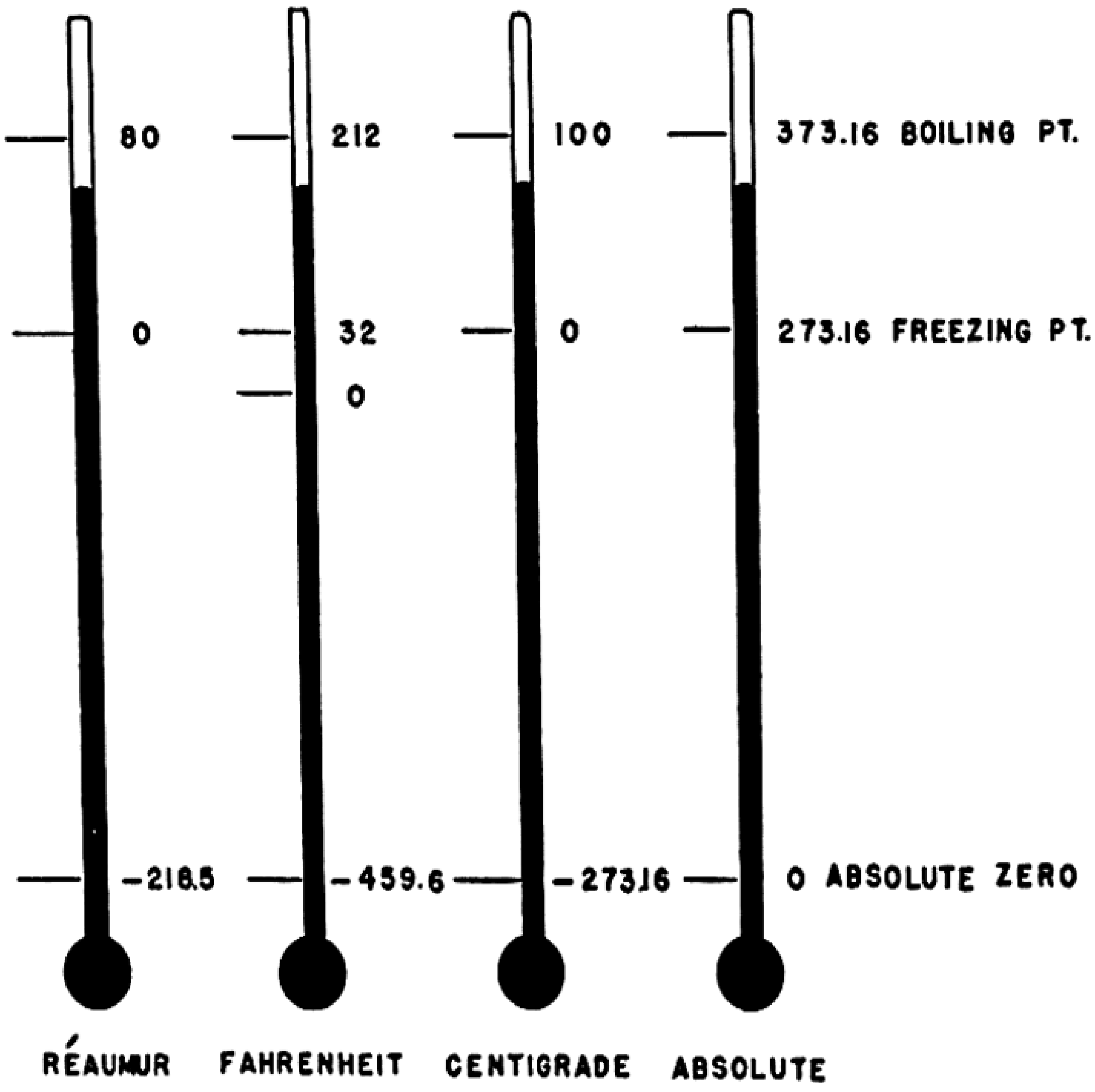

FIG. 2. Various scales of temperature.

Mercury Thermometers. Mercury boils at 356.7° C. and freezes at −38.9° C. and hence may be used between these limits as a thermometric fluid. The upper limit may be extended to above 600° C. by subjecting the mercury to an increased pressure. The volumetric coefficient of expansion is about 0.000181 per degree centigrade. When high pressures and temperatures are used, ordinary glass will soften, so quartz is used as the container for such thermometers.

Glass suitable for thermometers should possess a low and a constant coefficient of expansion. It should not soften at temperatures within the range to be measured. Most glasses show a hysteresis effect. That is, upon being heated and subsequently cooled they do not return exactly to their original volume, but are left slightly enlarged, resulting in a depression of the freezing point. Thermometers made of freshly blown glass develop scale errors due to a continued shrinkage of the glass. On this account the bulbs are usually aged, so that they have attained their constant volume before being filled.

For low temperatures, liquids other than mercury are commonly employed. Such liquids are acetone, toluol, alcohol, carbon disulphide, and pentane, whose freezing points are, respectively, about $-94°$ C., $-97°$ C., $-112°$ C., $-113°$ C., and $-200°$ C. In order that the thermometer may indicate the temperature to be measured as quickly as possible, it is desirable that the thermal conductivity of the materials of the container and the expanding fluid be large, and that the thermal capacity of the thermometer be small. This latter quantity depends upon the volume, the density, and the specific heat of the materials used. It is an interesting fact that the thermal capacity per unit volume of all the substances used in thermometers does not differ very much from 0.45 cal. per cm.^{3} per deg. C.

The Beckmann Thermometer. A mercury-in-glass thermometer capable of measuring very small temperature changes over a limited range was invented by E. O. Beckmann and is illustrated in Fig. 3. The bulb contains a large amount of mercury and the capillary tube is of small diameter such that a temperature change of 1 deg. will produce a motion of the mercury thread of about 4 cm. The total length of the scale is usually about 5 deg. In order that a single instrument may be used over a wide range in temperature a reservoir is provided at the top of the capillary tube for the superfluous mercury. It is thus necessary first to adjust the level of mercury to the desired working range. This is accomplished by heating the bulb to a temperature slightly greater than the desired value. Then as the bulb is allowed to cool a sharp lateral tap will break the mercury thread at the entrance to the reservoir. For lower temperatures, more mercury is needed in the bulb. As the bulb is heated the thermometer is inverted so that the mercury in the reservoir connects with the mercury in the stem. By carefully returning the thermometer to the upright position, as much mercury as desired may be drawn into the bulb.

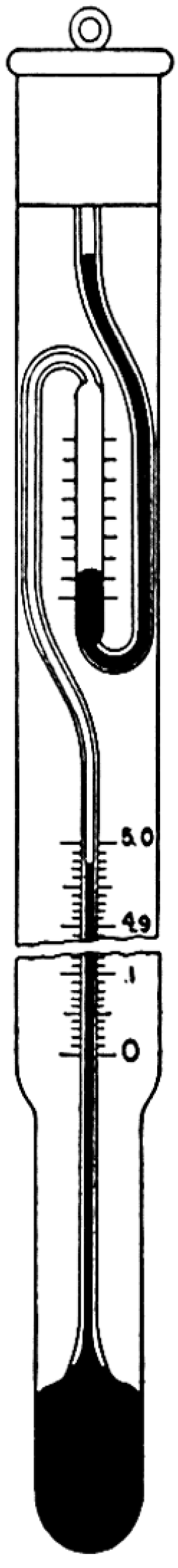

FIG. 3. The Beckmann thermometer.

Maximum and Minimum Thermometers. In order to find the maximum temperature that has been attained during a certain interval of time various types of maximum reading thermometers have been devised. A thermometer may be constructed with a constriction in the lower end of the capillary tube. The expanding mercury passes upward through the constriction, but on cooling the thread of mercury is retained in the capillary, indicating the highest attained temperature. The thermometer is reset by mechanical force. Clinical thermometers are of this type.

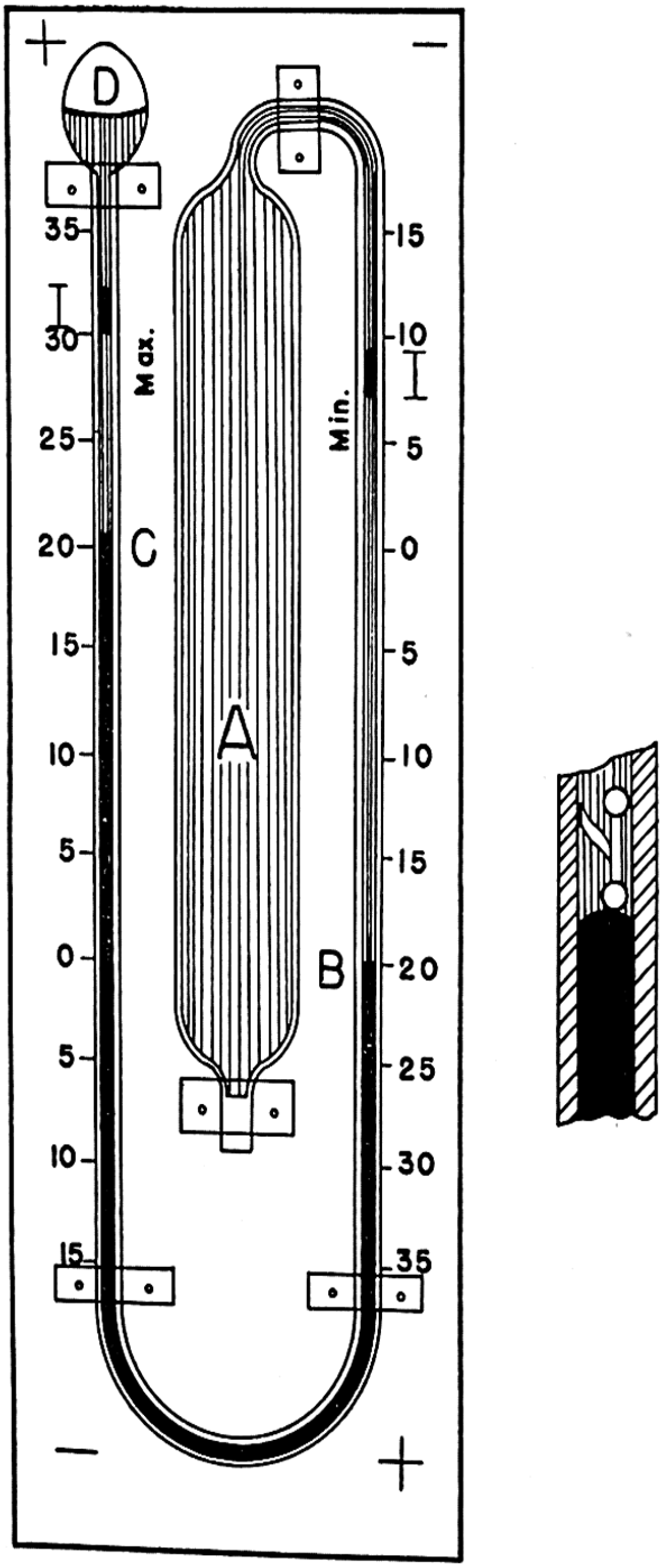

FIG. 4. The Six maximum and minimum thermometer.

One of the most extensively used arrangements, capable of indicating both the maximum and the minimum temperatures was devised by James Six and is shown in Fig. 4. The bulb *A* and part of bulb *D* are filled with a thermometric liquid such as alcohol. The connecting capillary tube contains a thread of mercury. Above the mercury on each side are small iron floats which serve as indexes of the temperatures. Each iron float is carried along by the advancing column of mercury but enough friction exists with the walls of the tube to allow it to remain in its highest position as the mercury recedes. The alcohol is able to pass freely by the stationary index. As the temperature is raised the expanding alcohol in bulb *A* compresses the gas in bulb *D* and thus pushes the mercury up in tube *C*, carrying along the index to give the maximum reading. At the same time the index on the right is left behind giving the minimum reading. A magnet is used to reset the indexes.

The Bourdon Thermometer. A mechanical device capable of indicating temperature by the change in shape accompanying the change in volume was invented by E. Bourdon. A flexible spiral-formed metal tube is filled with a liquid at a temperature lower than that at which it is to be used. As the temperature is increased the larger volume can be accommodated only by the unwinding of the tube, so that if one end is clamped, the motion of the free end may be arranged to move a needle over a scale indicating the temperature. Thermometers of this type have been extensively used in meteorological work and are readily adapted to recording devices. Owing to fatigue of the metal with continued distortion the thermometer should be frequently calibrated.

Bimetallic Strip Thermometers. If strips of two dissimilar metals having very different coefficients of expansion are riveted or welded together, a very useful item in thermometric work results. If bent into a spiral with the element of larger coefficient of expansion on the inside, then as the temperature is increased the spiral will unwind. If the end of the inside of the spiral is fastened, the resulting motion of the outer free end may be made to actuate a needle over a scale indicating the temperature. Similar arrangements are widely used in thermal controllers and recorders. Repeated use especially over a wide temperature range results in a permanent alteration of the spiral and necessitates frequent recalibration.

GAS THERMOMETERS

All gases have a much larger coefficient of expansion than the liquids usually used in thermometers. Many gases may be obtained in a pure state and are stable over a wide range in temperature. It is a natural consequence that thermometers should be constructed employing gases as the thermometric material. Although the early thermoscopes were in reality gas thermometers, they made use of neither a constant volume nor a constant pressure. Perhaps one of the first investigations dealing with the change in volume of a given amount of gas as the temperature was varied while the pressure was kept constant was carried out by J. A. C. Charles (1746–1823), a French physician, about 1780. He concluded that the relative increase in volume was the same for all gases for the same increase in temperature. More accurate investigations on the expansion of gases were carried out later by John Dalton (1766–1844), an English scientist, and by L. J. Gay-Lussac (1778–1850) and H. V. Regnault (1810–1878), French scientists. Experiments dealing with the change in pressure of a given amount of gas under constant volume, as the temperature was increased, were carried out by P. von Jolly (1809–1884), a German mathematician, and by Regnault and P. Chappuis in France.

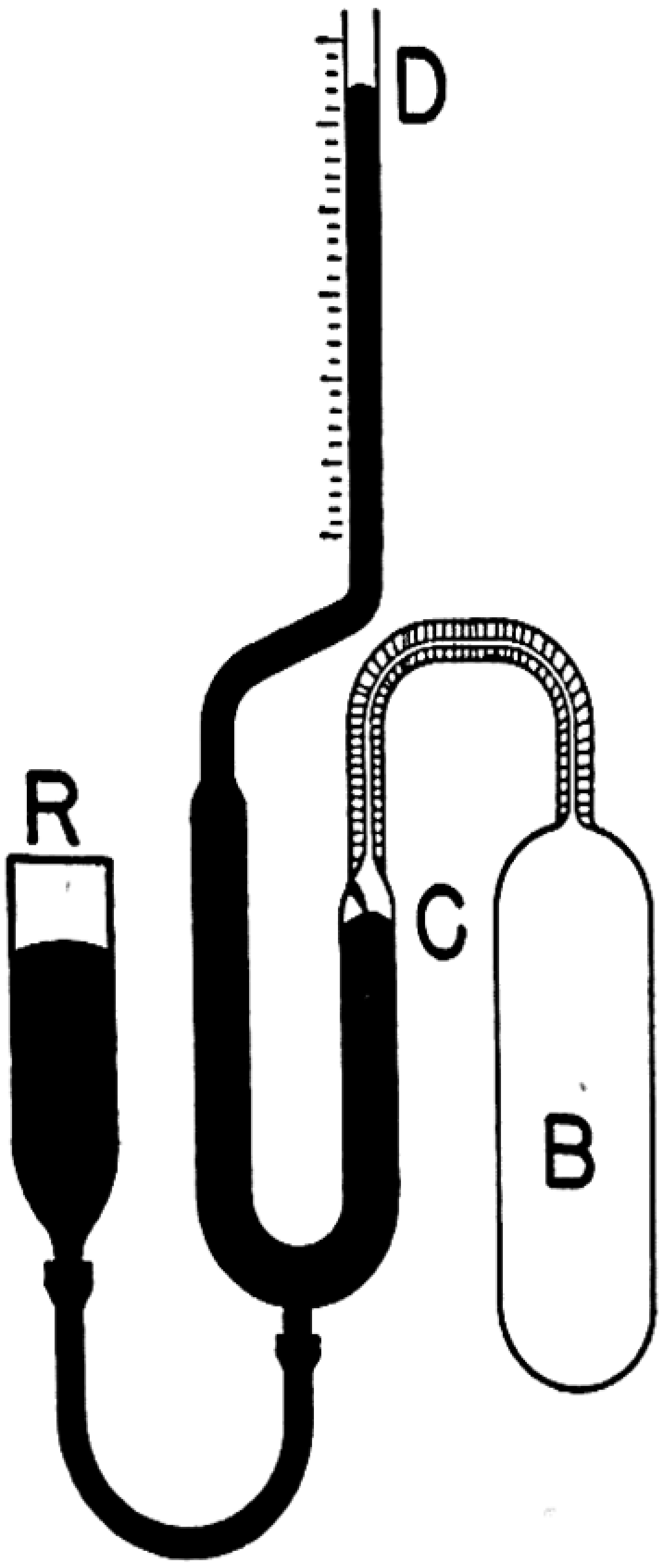

FIG. 5. Constant-volume gas thermometer.

The Normal Hydrogen Thermometer. At an International Congress on Weights and Measures held at Paris in 1887, it was agreed that the scale of temperature based upon the change in pressure of a constant volume of hydrogen under specified conditions should be considered fundamental. Preference was given to this device rather than the constant-pressure thermometer because of the very accurate work and the recommendation of Chappuis. The pressure of the hydrogen was prescribed as 100 cm. of mercury at the temperature of melting ice. The essential arrangement of the apparatus is as shown in Fig. 5. The large bulb *B* containing the pure hydrogen under the required pressure connects with the mercury manometer by means of a tube of very small volume. The level of mercury at *C* may be adjusted by raising or lowering the reservoir *R*. The pressure of the gas is then the difference between the levels *D* and *C* plus the pressure above *D*.

The fixed temperatures for the normal hydrogen thermometer were agreed upon as the boiling and freezing points of pure water under standard conditions. To measure an unknown temperature *X* with the normal thermometer, it becomes necessary to make three observations of pressure. These are, namely, the pressures with the bulb in melting ice, P_0, in boiling water P_{100}, and exposed to the unknown temperature X, P_x. The quantity $(P_{100} - P_0)/100$ is the change in pressure per degree change in temperature and may be represented by the symbol a. The temperature X is then given by the expression

$$X = \frac{P_x - P_0}{a} \tag{1}$$

This linear relationship which exists, by agreement, between the temperature and the pressure in the normal thermometer is shown in Fig. 6. This agreement may be formulated as follows: Those changes in temperature which produce equal changes in the pressure of a given amount of enclosed gas are to be regarded as equal intervals of temperature.

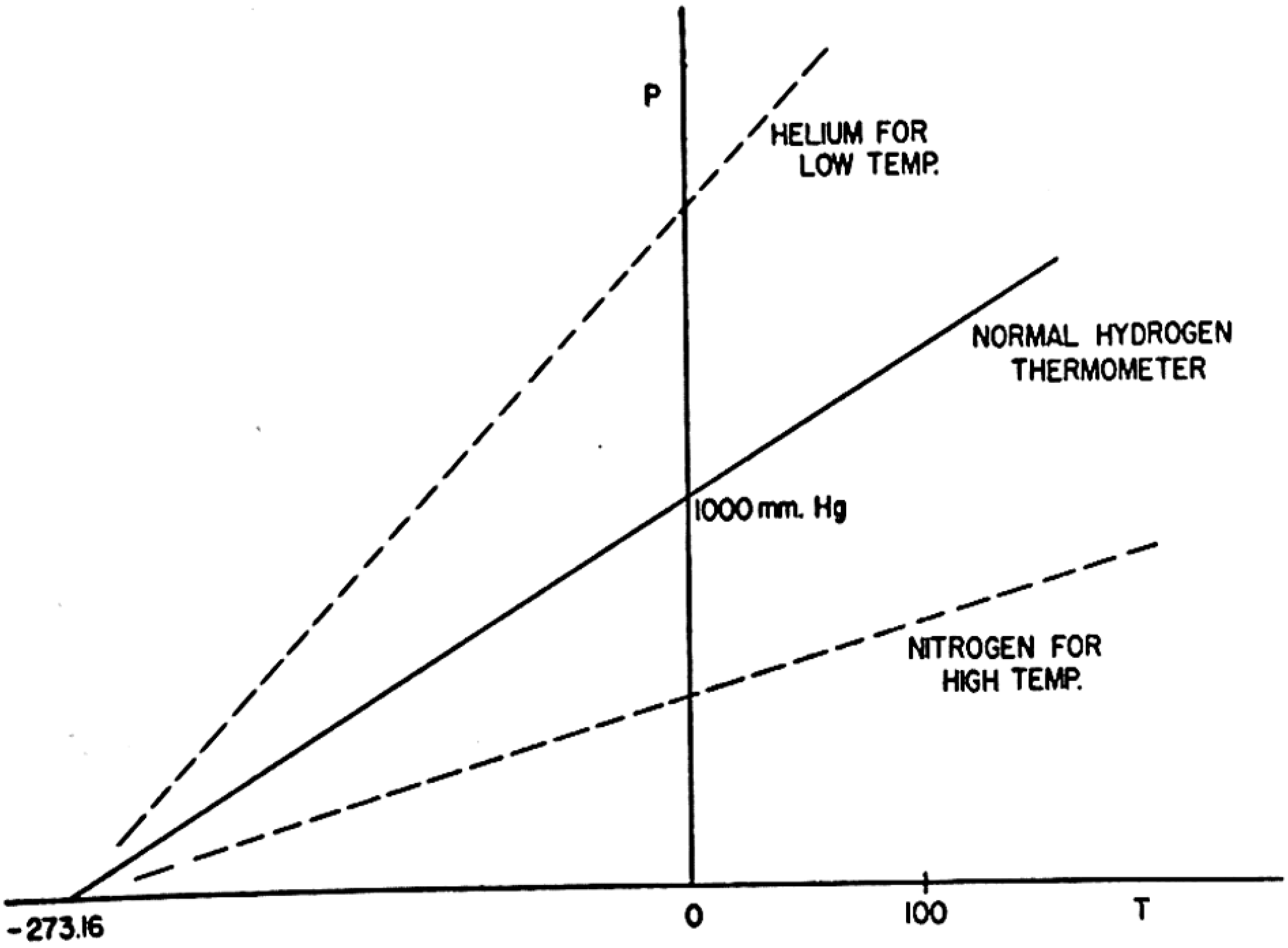

FIG. 6. Pressure-temperature relations for different initial pressures.

In actual practice it may be desirable to introduce certain modifications in the thermometer for convenience in manipulation. At high temperatures it is difficult to obtain a container impervious to hydrogen. On this account, nitrogen is often substituted for hydrogen in the thermometer. When the thermometer is to be used at high temperatures, the pressure of the gas at 0° C. may be adjusted to a value less than 100 cm. of mercury in order to avoid excessively high pressures. For the measurement of very low temperatures, helium is a more satisfactory gas than hydrogen. Whenever such modifications in the thermometer are employed, it becomes necessary to apply suitable corrections to the observed temperatures. The behavior of the gases for these different starting pressures is shown in Fig. 6. In each the pressure drops to zero at −273.16° C.

Corrections to the Observations of the Normal Thermometer. As the temperature of the bulb containing the gas is raised, the actual volume of the bulb increases, for two reasons. This enlargement is due in part to the thermal expansion of the material of the bulb, and also in part to the fact that at the higher temperature the confined gas is at a higher pressure, thereby causing an elastic expansion of the bulb. This elastic enlargement may be prevented by using as a source of temperature a chamber so constructed that the pressure within it may be adjusted to any desired value. It is thus possible to make the pressure outside the thermometer bulb approximately equal to that within.

An added error arises from the fact that the connection between the bulb and the manometer possesses a small distributed volume v called the "dead space." The gas in this volume is not subject to the variation in temperature of the bulb. Consequently, as the temperature of the bulb is increased, some additional gas is forced into the "dead" volume. Assuming the temperature of the dead space to remain constant, at a value T', then the true temperature T to which the bulb is exposed may be found from an expression equating the total mass of gas in the bulb and dead space before heating to that after heating. This expression is somewhat simplified by assuming 0° C. as the original temperature of the bulb.

Denoting the density, volume, and pressure of the gas at 0° C. as ρ_0, V_0, and P_0, respectively, the pressure at T° C. as P, the coefficient of volumetric expansion of the material of the bulb as g and that for the gas as β, then it follows that:

$$V_0\rho_0 + v\frac{\rho_0}{1+\beta T'} = \frac{\rho_0 V_0(1+gT)}{1+\beta T}\cdot\frac{P}{P_0} + \frac{v\rho_0}{1+\beta T'}\cdot\frac{P}{P_0} \tag{2}$$

By introducing ΔP for $(P - P_0)$ and solving for T, it follows that:

$$T = \frac{\Delta P\left[1 + \frac{v}{V_0} + \beta T'\right]}{\beta P_0\left[1 - \frac{Pg}{P_0}(273 + T') - \frac{\Delta P}{P_0}\cdot\frac{v}{V_0} + \beta T'\right]} \tag{3}$$

Equation 2 may equally well be solved for β, giving:

$$\beta = \frac{\Delta P\left(1 + \frac{v}{V_0} + \frac{P}{\Delta P}gT\right)}{P_0T\left(1 - \frac{P}{P_0}\cdot gT' - \frac{\Delta P}{P_0}\cdot\frac{v}{V_0} + \beta T' - \frac{\Delta P}{P_0}\cdot\frac{T'}{T}\right)} \qquad (4)$$

from which a value may be obtained by successive approximation. Thus this device may be employed to measure the thermal coefficient of expansion of the gas as well as to measure temperature.

Vapor Pressure Thermometers. The pressure of a saturated vapor in equilibrium with the same substance in the liquid state is a definite function of the temperature and changes rapidly with any change in temperature. By establishing the exact relationship between the vapor pressure and the equilibrium temperature it becomes possible to utilize this property to measure temperature. Mathematical expressions representing the relationship between the vapor pressure and the temperature are discussed later on page 199. The graphical representations of this relationship for helium, hydrogen, neon, nitrogen, and oxygen are shown in Fig. 7.

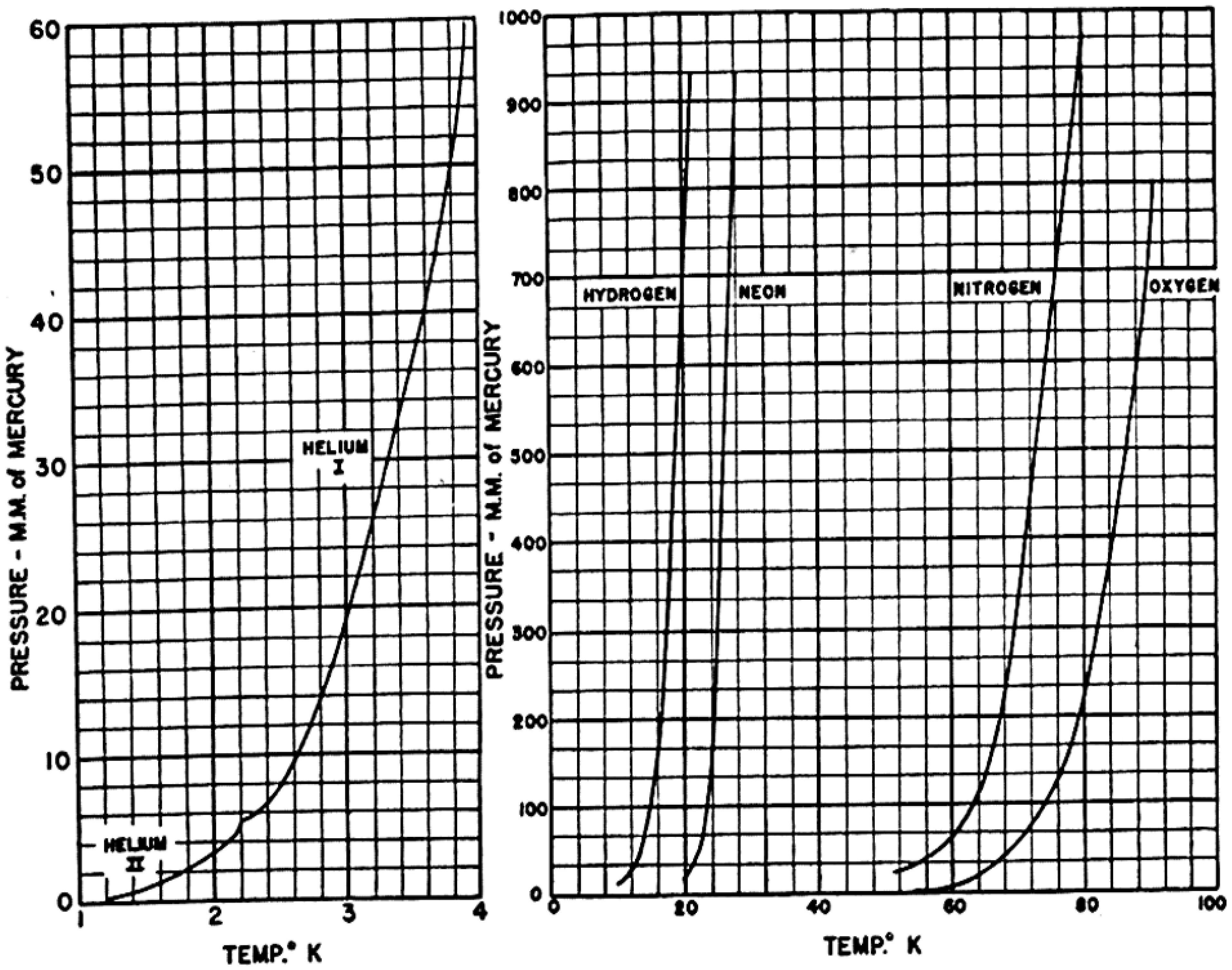

FIG. 7. Saturated vapor pressure curves for several elements.

Vapor pressure thermometers have certain favorable characteristics. A large change in pressure is associated with a relatively small change in temperature, so that a high sensitivity results. The pressure developed is independent of the amount of liquid present and of any characteristic of the container except its vapor pressure. This information on vapor pressure is of value in the field of extremely low temperatures, since the temperature of a boiling liquid serving as a bath can be adjusted to any desired value by a suitable adjustment of the pressure to which it is exposed.

RESISTANCE THERMOMETERS

It was proposed[8] by Sir William Siemens (1823–83), a German engineer living in England, in 1871, that the change in electrical resistance in a metallic conductor that accompanies the change in temperature might serve to measure the temperature. A device of this sort may be termed a resistance thermometer.

The Platinum Resistance Thermometer. Since platinum does not oxidize at high temperatures and since it has a rather uniform change in resistance with temperature over a wide range, it is well adapted for use in the elements of resistance thermometers. In the early coils made by Siemens, the platinum wire was wound on a clay form and the assembly placed in an iron protecting tube. When heated, an impurity was absorbed by the platinum causing a change in resistivity. On this account thermometers of this type were not used extensively until after 1886 when their construction was improved by H. L. Callendar.[9]

To determine an unknown temperature, measurements are first made of the resistance of the element of the thermometer at the two fixed temperatures 0° C. and 100° C. These resistances are termed respectively R_0 and R_{100}. Now if the relationship between the resistance R and the temperature T is linear, then, on a resistance-temperature plot, a straight line may be drawn through these points, as shown in curve A, Fig. 8. The equation representing this straight line may be written as:

$$R_T = R_0(1 + \alpha_0 T) \tag{5}$$

in which $R_0\alpha_0$ represents the slope of the curve, and R_T is the resistance at any temperature T. The quantity α_0 as so defined is called the zero thermal coefficient of resistance. The actual relationship existing between the resistance R and the temperature as measured by the " normal " thermometer is indicated in Fig. 8 by curve B. For pure platinum it has been found that the relationship between the resistance and the temperature may be satisfactorily represented by the following parabolic equation where T is the true temperature and α and β are empirical constants:

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[8] W. Siemens, *Proc. Roy. Soc.* (*London*), **19**, 443 (1871).

[9] H. L. Callendar, *Roy. Soc. Phil. Trans.* (*London*), **178**, 161 (1887).

$$R_T = R_0(1 + \alpha T + \beta T^2) \tag{6}$$

Values of $\alpha = 0.00392$ and $\beta = -0.000000588$ represent well the performance of platinum for temperatures between −40° C. and 1,000° C. To calibrate the thermometer an additional known temperature must be employed. The normal boiling point of sulphur (444.60° C.) is often used in this case. The correction to the boiling point of sulphur for pressures less than 760 mm. is approximately −0.091° C. per mm. The boiling point of naphthalene, 217.96° C., with a correction of −0.058° C. per mm., is also a convenient temperature for calibration. Temperatures which are calculated by employing the assumed relationship of curve A, Fig. 8, are called "platinum" temperatures. Callendar[10] deduced a simple expression so that the true temperature T could be readily obtained from the platinum temperature T_{Pt}. The value of the resistance at any true temperature T is

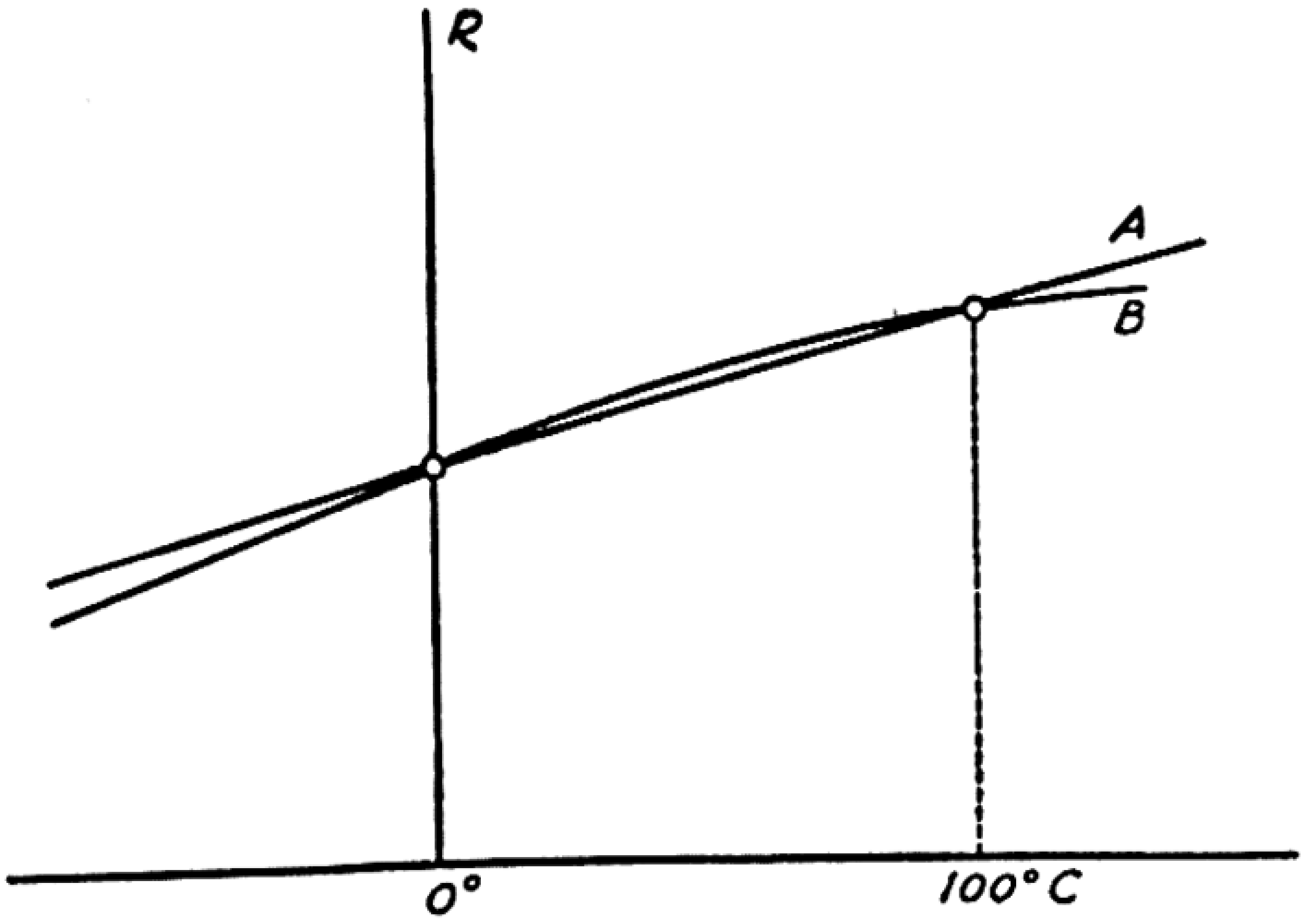

FIG. 8. Resistance-temperature relationship for platinum: A, hypothetical; B, actual.

$$R_T = R_0(1 + \alpha_0 T_{Pt}) = R_0(1 + \alpha T + \beta T^2) \tag{7}$$

At the boiling point of water $T = T_{Pt} = 100$, so that $\alpha_0 = \alpha + 100\beta$. On substituting this in equation 7 and rearranging

$$T - T_{Pt} = \frac{(100)^2\beta}{\alpha + 100\beta}\left[\frac{T}{100} - \frac{T^2}{(100)^2}\right] = \delta\left[\frac{T}{100} - \frac{T^2}{(100)^2}\right] \tag{8}$$

The value of the constant δ for platinum is found to be about −1.5, varying somewhat with the purity of the specimen. Other metals sometimes employed in resistance thermometers are palladium and nickel.

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[10] H. L. Callendar, *Roy. Soc. Phil. Trans. (London)*, **178**, 161 (1887).

Measurement of Resistance. Many types of Wheatstone and Kelvin bridges have been designed especially for use with resistance thermometers. These bridges are generally operated with a one to one value for the ratio arms. In this way it is possible to compensate for variations in the resistance of the wires connecting the platinum coil to the bridge. This is essential, since these connecting wires are subjected throughout their length to temperatures which may not be known. No variable contact resistance should be allowed in series with the thermometer. Moreover, the measuring current must be limited to a small value in order that it may have no influence on the temperature of the thermometer. Figure 9 illustrates a resistance bridge as used by Callendar in which the " three-wire " method of connecting the resistance thermometer T is employed. The connecting wires are labeled 1, 2, and 3, and they are identical in dimensions. By connecting the battery B to wire 2, wire 1 is thrown in series with the resistance R_1 in the bridge while wire 3 is in series with the platinum coil T. Now any change in temperature in wire 3 is fully compensated by a similar change in wire 1. By the proper design of the arc D, changes equivalent to a variation of 0.0001 ohm in the resistance thermometer may be read directly.

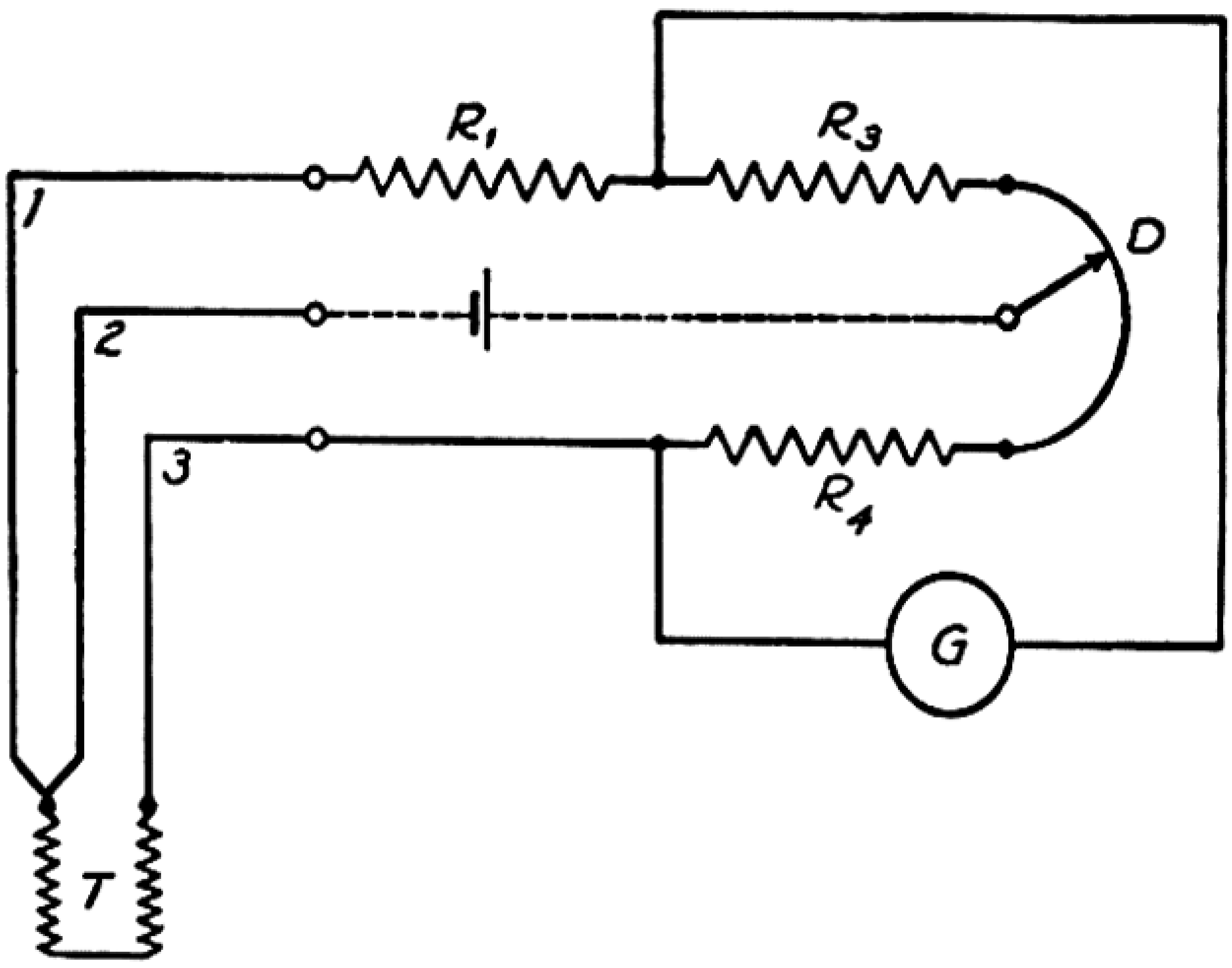

FIG. 9. Resistance thermometer bridge — three-wire compensation (Callendar).

Many other arrangements may be employed to compensate properly for variations in the resistance of the connecting wires.

A commonly employed circuit known as the four-wire dummy-pair method consists of four parallel identical wires, only two of which are connected to the thermometer terminals. The other pair of wires fastened together at their distant ends, lie beside the thermometer leads but are electrically insulated from them. This dummy pair is connected in series with the fixed resistance of the bridge, such as R_1 in Fig. 9. Thus any alteration in the resistance of the actual thermometer leads is completely offset by the same change in the resistance of the dummy pair.

The Bolometer. A resistance thermometer of very great sensitivity was used by Langley[11] in 1881. This was designed so that it could be used to measure relatively the distribution of energy in the spectrum of the radiation from a hot body and was called a bolometer. As used by Lummer and Kurlbaum[12] in 1892, this device was constructed by stamping from a thin platinum foil four grids, each being as shown in Fig. 10. By arranging these grids in pairs, the open space in one was completely covered by the material of the other. One of these grids was made to form the arm T, and the other of the overlapping pair became R_3 in a resistance bridge as shown in Fig. 9. The other two grids comprising the other arms in the resistance bridge were maintained at a constant temperature. This arrangement is shown in Fig. 11. With no radiation incident upon the grids, the bridge was balanced. Now upon exposure to radiation the resistances R_3 and T both increased, each tending to unbalance the bridge in the same direction, thus yielding an additive effect. By this means changes in tem-

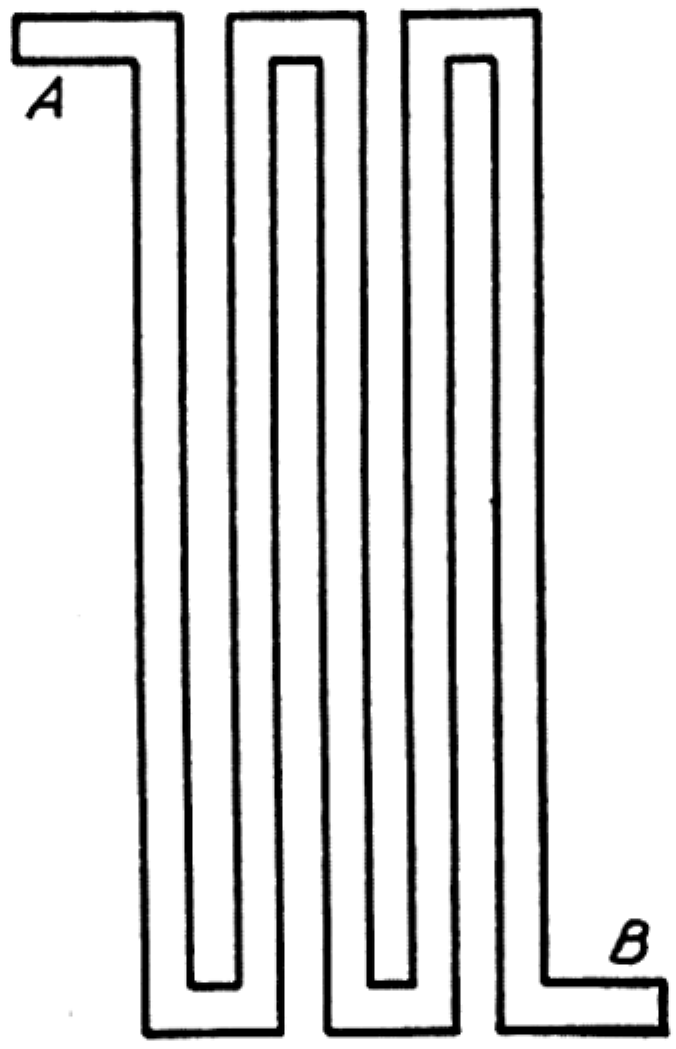

FIG. 10. Stamping of platinum foil for element of bolometer.

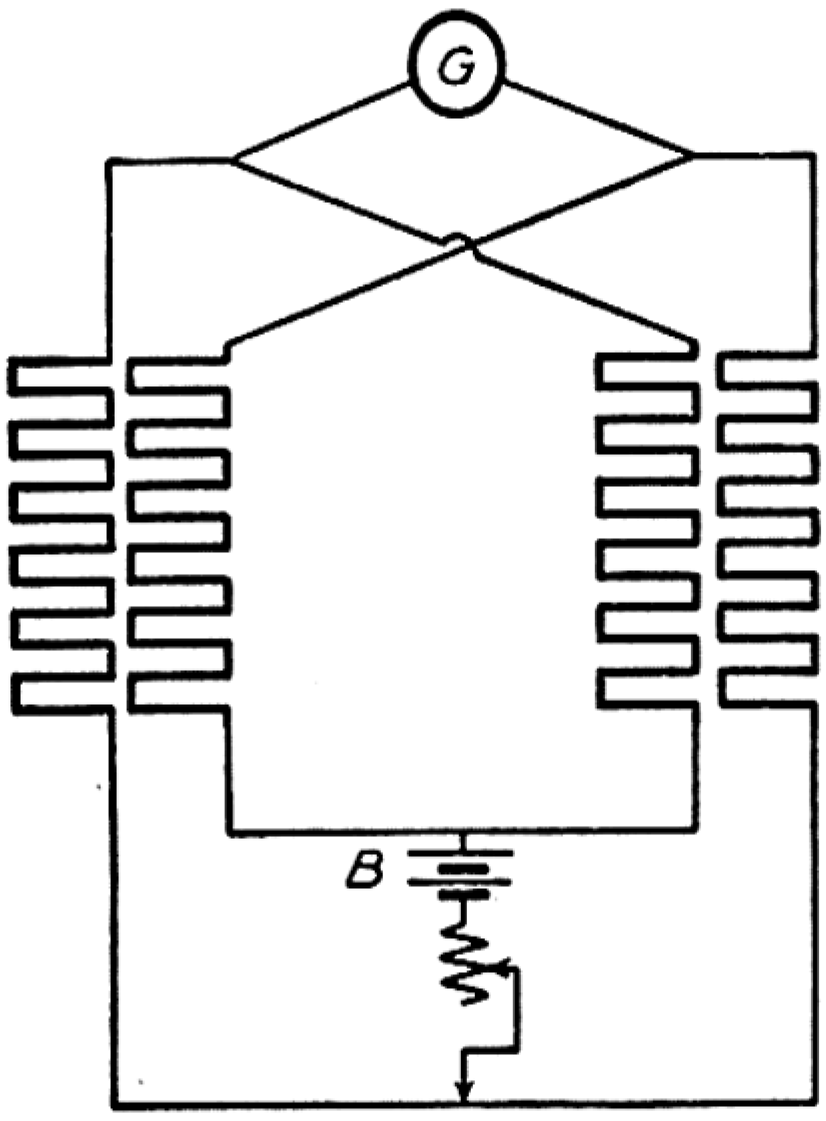

FIG. 11. Bolometer bridge (Langley).

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[11] S. P. Langley, *Am. Jour. Sci.*, **21**, 187 (1881).

[12] O. Lummer and F. Kurlbaum, *Ann. Physik.*, **46**, 204 (1892).

perature as minute as 0.0001° C. could be detected, and by using very thin foils the thermal capacity of the receiver was so small that temperature equilibrium was quickly obtained.

THERMOELECTRIC TEMPERATURE MEASURING DEVICES

Thermal Electromotive Forces. It was discovered by Seebeck[13] in 1821, that when wires of two unlike metals were fused together at one end and heated, an electromotive force existed between the other ends of the two wires. When the two wires were copper and iron, by connecting a galvanometer in the circuit a current was found to flow continuously from the iron to the copper. By arranging an additional junction of the same materials in series as shown in Fig. 12 and maintaining the junctions at unlike temperatures, T_0 and T respectively, then the electromotive force developed in the system may be expressed in terms of the difference in temperature between the hot and cold junctions $(T - T_0)$. If the temperature of the colder junction be kept at 0° C., then for many pairs of metals the emf. developed is almost proportional to T.

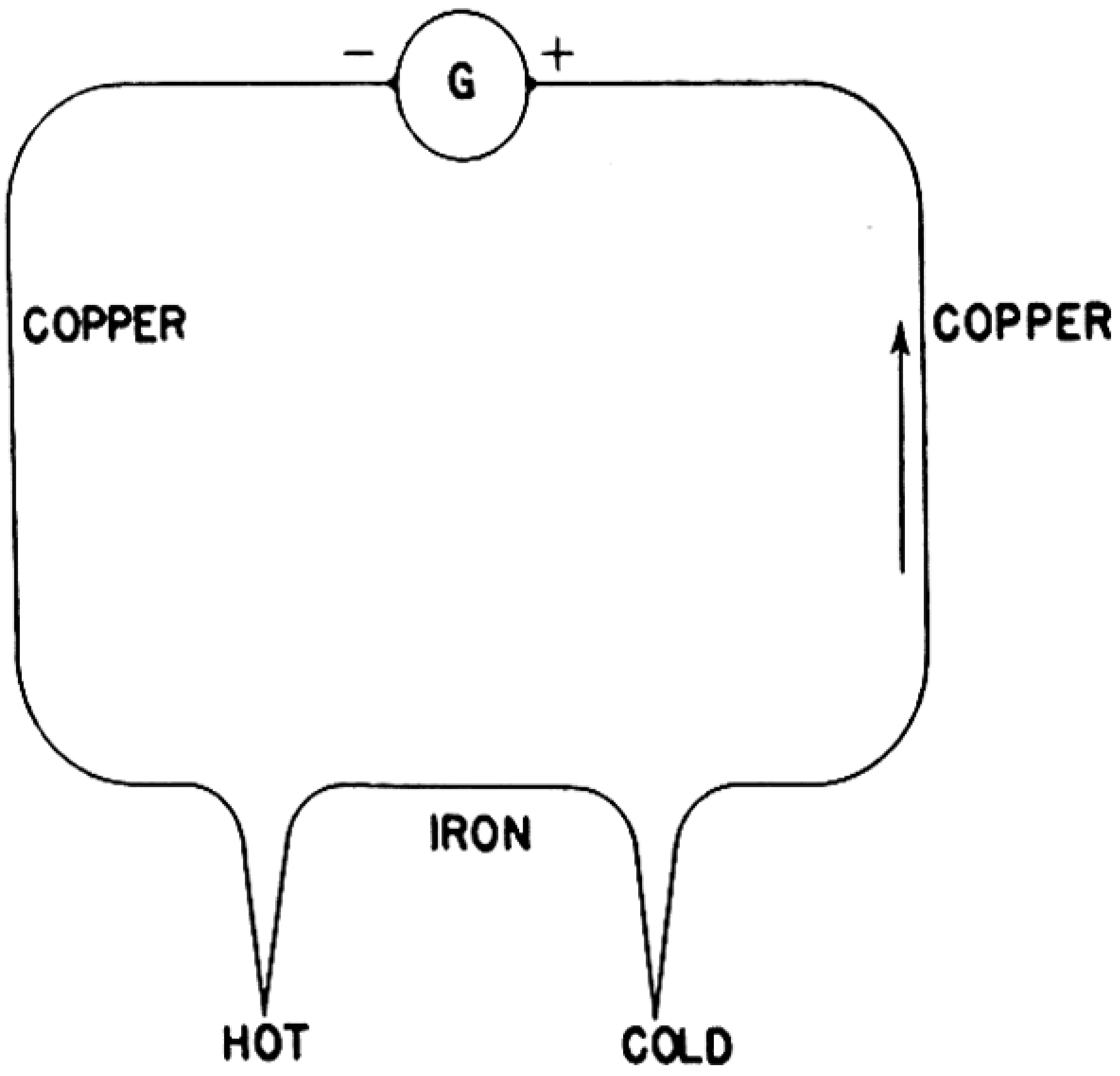

FIG. 12. Thermocouple circuit with galvanometer

Thermocouples. Although a junction of any two dissimilar metals will yield a thermal electromotive force when heated, the term " thermocouple " is usually restricted to those junctions capable of being employed in the measurement of temperature. One such pair of metals consisting of a pure platinum wire and another wire composed of 90% platinum and 10% rhodium, called a " noble " metal couple, was developed by Le Chatelier.[14] Many other pairs of "base" metals have been found to be very satisfactory for thermocouples. Such combinations often employed are iron and constantan, chromel and alumel, copper and constantan, and chromel with copel. Constantan is an alloy of 60% copper and 40% nickel; chromel is 90% nickel and 10% chromium; alumel is 2% aluminum, 3% manganese, 1% silicon, and 94% nickel; and copel is an alloy of 45% nickel and 55% copper.

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[13] T. J. Seebeck, *Pogg. Ann.*, **6**, 133, 263 (1826).

The actual relationship between the electromotive force E and the temperature T may usually be very well represented by an empirical equation as

$$E = a + bT + cT^2 \qquad (9)$$

where a, b, and c are empirical constants.

The derivative of this expression with respect to temperature, that is, dE/dT, usually expressed in microvolts per degree, is called the thermoelectric power of the couple (although lacking the fundamental dimensions of power). The thermoelectric power of most base-metal couples is about five times that of the noble-metal couple. The average values between 0° C. and 1,000° C. for platinum versus 90% platinum −10% rhodium, chromel versus alumel, and iron versus constantan couples are respectively 9.57, 41.3, and 58.1 microvolts per degree centigrade. For temperatures above 1,000° C. only noble

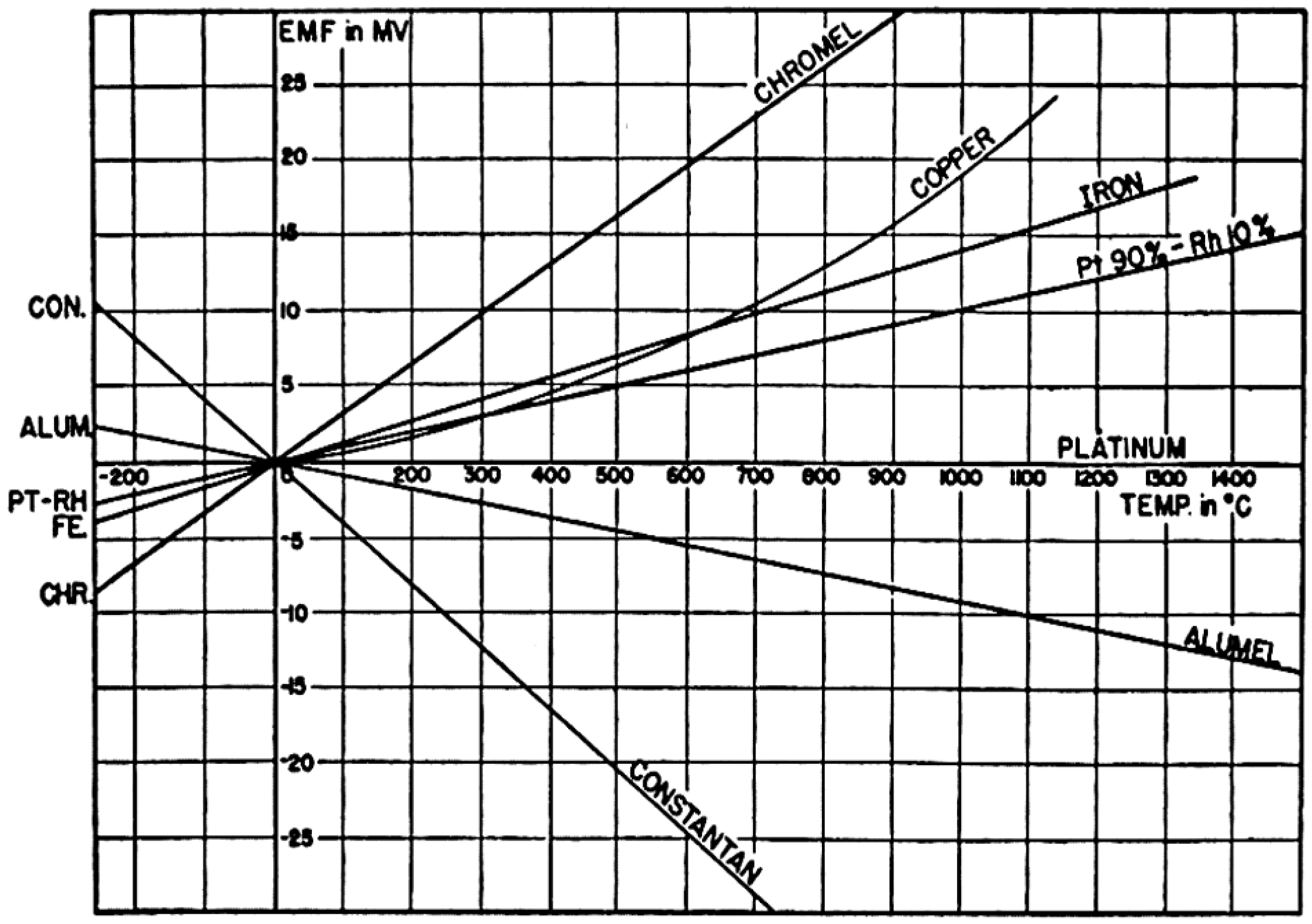

FIG. 13. Thermal electromotive forces of various elements with platinum.

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[14] H. Le Chatelier, *Compt. rend.*, **102**, 819 (1886).

metals are satisfactory. The relationship between emf. and temperature for the noble-metal couple and the base-metal iron-constantan and chromel-alumel couples are given in the Appendix, Tables 20 to 25. Figure 13 shows the emf.-temperature relationship for several materials with respect to pure platinum. Electromotive force is positive in the upward direction. It is thus possible to predict the performance of a thermocouple made from any pair of these metals.

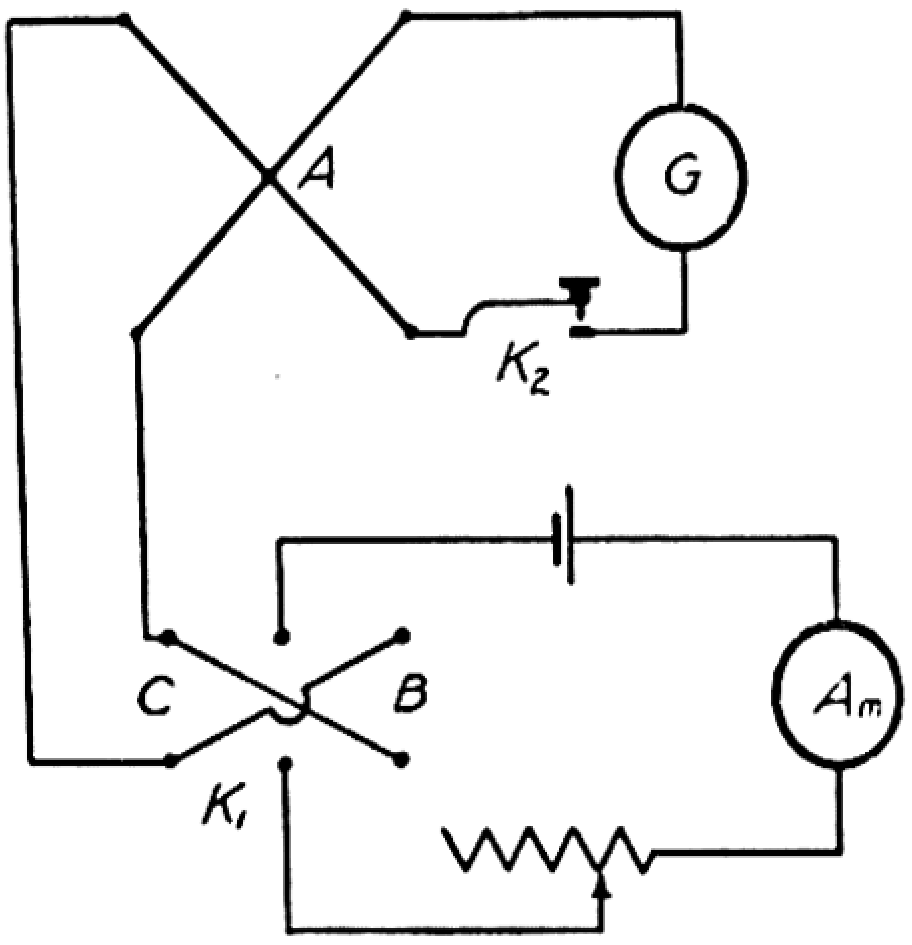

FIG. 14. Apparatus to demonstrate the Peltier effect.

The Peltier Effect. The location of the source of the thermal emf. naturally became a subject for speculation. It was observed by Peltier[15] in 1834 that, when an electric current was passed through the junction of two metals, there resulted either an absorption or an evolution of heat, depending upon the direction of the current. This indicated the existence of an emf. at the common surface of the two metals. When the current is made to flow against this emf. a heating in excess of that due to the ohmic resistance of the conductor will result. When the current flows in the direction of the emf. a cooling effect will be present. This effect may be readily demonstrated by the apparatus shown in Fig. 14. Two metal wires of large size, made of materials such as iron and constantan, are fused at A. With the switch K_1 at B a current I is made to pass through A. By opening K_1 and quickly closing K_2 the galvanometer G is connected to the junction A. A following trial may be made with a reversed current through A by changing K_1 to the position C. In one position of K_1 a decided heating effect at A will be observed since the ohmic heating and the Peltier effect add. In the other position their difference is observed, which may be either a resultant heating or cooling effect. By suitably adjusting the current I it is possible to have the cooling effect predominate. A Peltier coefficient π, characteristic of a pair of metals at a definite temperature, may be defined as the heat H liberated per unit of electrical charge e transported, that is, $\pi = dH/de$. It is shown later from thermodynamic reasoning, page 241, that π may be found by forming $T(dE/dT)$ in equation 9.

The Thomson Effect. In a circuit made up of wires of dissimilar metals, the existence of emf.'s other than those at the junctions was

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[15] A. Peltier, *Compt. rend.*, **1**, 360 (1835).

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discovered by Thomson[16] (Lord Kelvin) (1824–1907). An examination of this effect led to the conclusion that in general an emf. exists between any two regions at different temperatures in a single conductor. The existence of this effect may be demonstrated by the apparatus shown in Fig. 15. In this arrangement a heavy wire *mn*, capable of carrying a large current, is heated at its central section *H*. In two symmetrically placed drill holes *a* and *b* are placed insulated thermojunctions connected differentially to a galvanometer *G*. Fused sulphur makes a satisfactory insulator between thermojunctions and wire. With the switch open so that the wire *mn* is carrying no current the galvanometer may be made to read zero by sliding the heater *H* along the rod. Then *a* and *b* are at the same temperature. Now upon closing the switch and sending a current through the bar a steady state will soon be attained in which the galvanometer shows a steady deflection. Thus although the heating effect of the current might have been expected to change the temperature of *a* and *b* equally, some other effect was present causing them to assume different final values. Upon reversing the direction of the current a steady state will be attained in which the galvanometer deflects in the opposite direction. These results may be satisfactorily explained by assuming that a potential gradient exists between the hotter region at the center of the bar and the cooler regions on either side. Then on one side of the center the electric current will have the direction of the potential gradient and will produce a cooling effect while on the other side the current flows in a direction opposite

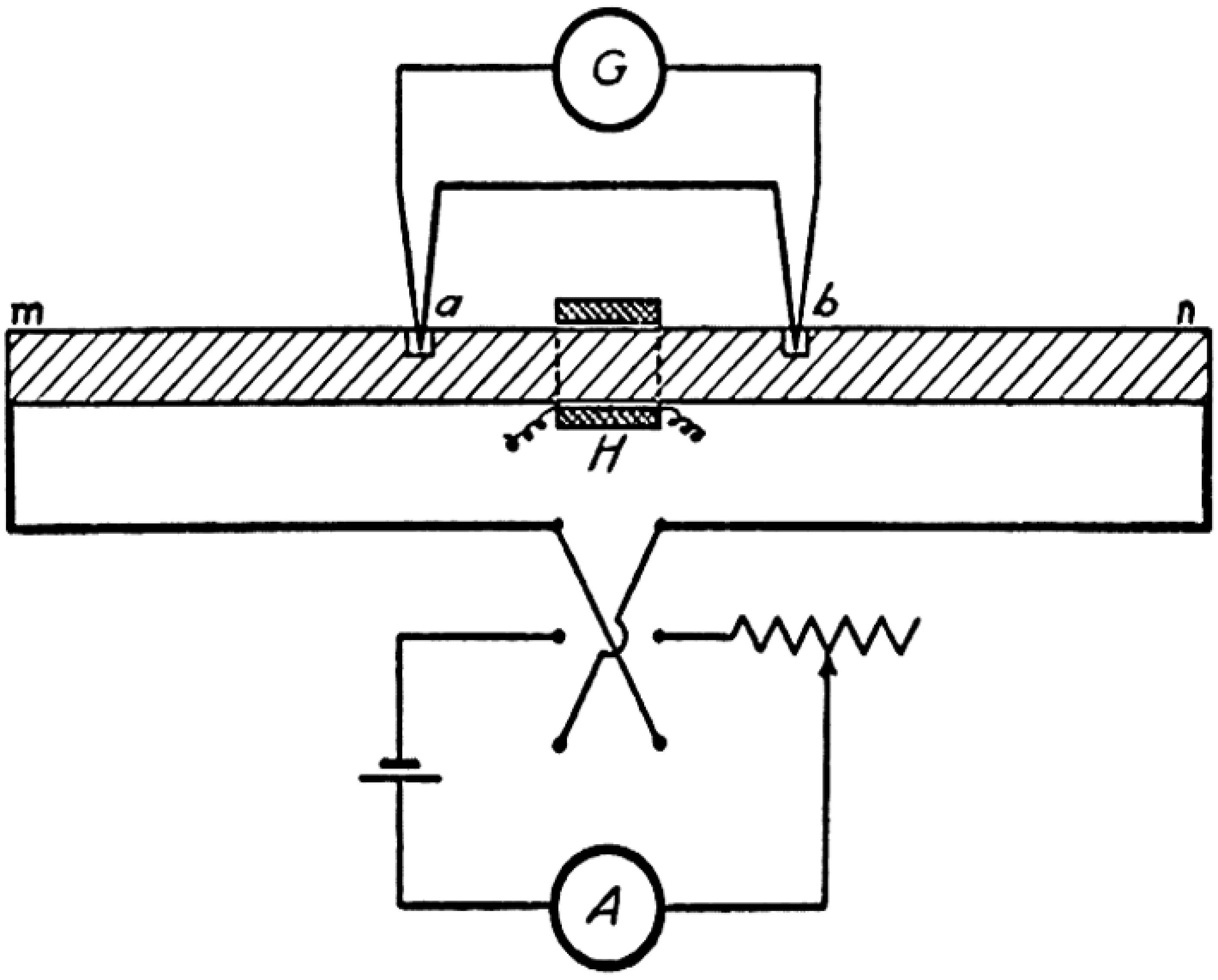

FIG. 15. Apparatus to demonstrate the Thomson effect.

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[16] W. T. Thomson, *Trans. Roy. Soc.* (*Edinburgh*), **21**, 123 (1854), *et seq.*

to the thermal potential gradient and results in an added heating effect. The heat absorbed or released H is proportional not only to the quantity of electricity e transferred but also to the difference in temperature, so that a Thomson coefficient τ may be defined such that

$$\tau = \frac{1}{e} \cdot \frac{dH}{dT} \quad \text{or} \quad H = \int_{T=T_1}^{T=T_2} e\tau dT \tag{10}$$

From thermodynamic reasoning, page 242, it is shown that the difference in the two Thomson coefficients characteristic of the metals of a thermocouple may be expressed in terms of the developed electromotive force E as

$$\tau_a - \tau_b = T\frac{d^2E}{dT^2} \tag{11}$$

If τ is positive, then a positive electric current from the hot section to the cooler portion tends to make the temperature uniform. It is as if the electricity had a certain "specific heat." It is possible to express the Thomson coefficient empirically by an equation of the form

$$\tau = \alpha + \beta T \cdot 10^{-2} + \gamma T^2 \cdot 10^{-5} \tag{12}$$

where T is in centigrade degrees and the constants, α, β, and γ have the values shown in Table 1 for certain common metals.

Nature of Thermoelectric Effects. Any sufficient theory of electric conduction in metals must equally well allow for the existence of Peltier and Thomson emf.'s. The free electron theory of metallic conduction does this in a satisfactory manner. If N stands for the number of free electrons per cubic centimeter, U the average velocity of the electrons, e their electric charge, l their mean free path, k the gas constant per particle, and σ the electrical conductivity, then (see equation 55, Chapter IV)

$$\sigma = \frac{e^2}{6k} \cdot \frac{NlU}{T} \tag{13}$$

Now N, l, and U may all be regarded as changing with T. Larger values of l, N, and U would favor the migration of electrons from a region. At increased temperatures, however, l decreases while N and U probably increase. It is thus possible to see that at certain temperatures the Peltier and Thomson effects, characteristic of a particular element, might actually reverse, a fact observed for many metals.

Potential Measurement. Potential indicators may be either deflection instruments (millivoltmeters) or potentiometric devices. The latter type draw no current from the source of emf., and hence their

TABLE 1

CONSTANTS IN THE EQUATION FOR THE THOMSON COEFFICIENT

Substance	Temperature Range		α	β	γ
	Low	High			
Aluminum	−13	119	−0.04	−0.475	
	71	322	0.268	0.080	
Bismuth	25	32	6.76	2.8	
Constantan	87	480	20.0	2.55	−10.05
Copper	−172	−60	−2.244	−2.5	−6.4
	−60	130	−1.42	−0.74	
	250	680	−1.37	−0.235	
Iron	−50	115	4.00	8.4	
	90	440	7.78	8.61	
Lead	45	340	0.03	−0.47	0.55
Platinum	−70	130	9.10	−0.475	4.75
Silver	−160	−120	−0.112	9.47	42.0
	120	520	−3.08	−3.02	
Tin	−170	110	−0.09	0.50	
	50	250	0.35	0.093	

readings are not influenced by any variation in the electrical resistance of the thermocouple. The electromotive forces to be measured in work with thermocouples are small; for example, a noble-metal couple has a thermoelectric power of only about 9 microvolts per degree. Satisfactory potentiometers thus must be designed to measure with accuracy variations in emf. less than 1 microvolt.

The Thermopile. To detect very small changes in temperature, several thermocouples may be arranged in series forming a "thermopile." The elements, if made of antimony and bismuth alloys, exhibit a remarkably large thermoelectric power and when used in conjunction with a sensitive galvanometer, result in an indicator of extreme sensitivity. Thermopiles of this type have been described by A. H. Pfund.[17] By arranging the hot junctions back of the final slit of a spectrometer exposed to a source of radiation, this device is able to reveal the distribution of energy as a function of the wavelength of the spectrum such as shown in Fig. 16.

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[17] A. H. Pfund, *Rev. Sci. Inst.*, **8**, 417 (1937).

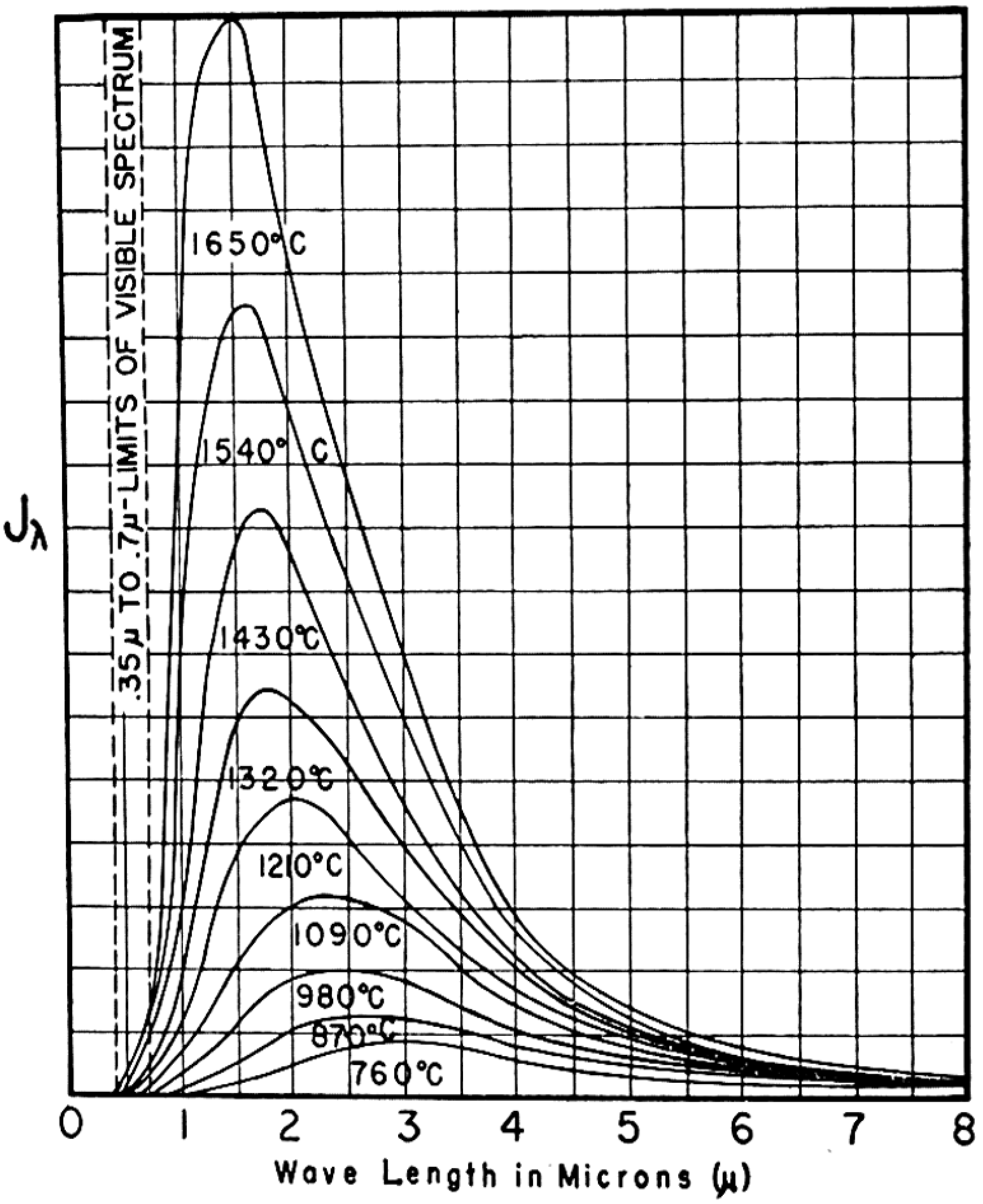

FIG. 16. Radiation from a black body at various temperatures.

OPTICAL PYROMETERS

Temperature and Color. The color of a body when it is due to emitted light is dependent upon the wavelength or combination of wavelengths in the radiation coming from it to the eye. To be visible some radiation of wavelengths between about 3,500 Å (0.000035 cm.) and 7,000 Å (0.00007 cm.) must be present. At a temperature of about 475° C., heated bodies become visibly red. As the temperature is increased, the radiation includes relatively more energy in shorter wavelengths, so that at about 1,000° C. the color of the body might be termed yellow, at about 1,200° C. it has a whitish yellow appearance, and at still higher temperatures the appearance may be described as bluish white.

Black-Body Radiation. The temperature of a body does not alone determine the amount of radiant energy emitted per unit area per second from its surface. Thus if identically shaped bodies of polished platinum and carbon are heated to the same temperature the emission from the carbon may be many times that from the platinum. However, if the two bodies are placed in a uniformly heated enclosure and observed through a minute opening, then the radiations from the two bodies are identical. The platinum makes up, by reflection, for that radiation which was lacking in its pure emission. This enclosure with the small opening may be called a " black body " since any radiation incident from outside upon the opening will be completely absorbed.

The radiations from the aperture of the enclosure are dependent only upon the uniform temperature within. The distribution of energy in this radiation with respect to wavelength and temperature has been very accurately determined by Lummer and Pringsheim[18] and others.[19] The results of these investigations are shown in Fig. 16. From these observations certain generalizations called the " laws of black-body radiation " may be deduced. These relationships are discussed in detail in Chapter V. For the present consideration only the final results are important.

For the intensity of radiation J_λ as a function of the wavelength λ and the temperature T, the following two relationships have been developed:

$$\text{(Wien)} \quad J_\lambda = C_1\lambda^{-5}e^{-C_2/\lambda T} \tag{14}$$

and

$$\text{(Planck)} \quad J_\lambda = C_1\lambda^{-5}(e^{C_2/\lambda T} - 1)^{-1} \tag{15}$$

In both equations 14 and 15, C_2 is a fundamental constant of nature having the value 14,320 when λ is expressed in microns and T in absolute degrees. C_1 is a constant dependent upon the experimental arrangement.

The Disappearing-Filament Optical Pyrometer. When a valid relationship has been established between the intensity of radiation J_λ, the wavelength λ, and the temperature of the radiating body T, it becomes possible to use the measurement of J_λ to evaluate the temperature. Devices whose operation is based upon these relationships, i.e., the Planck law or the Wien law, are called optical pyrometers and were probably first employed by Le Chatelier[20] in 1892. As ordinarily used, they have the form of an optical telescope provided with certain additional parts. The arrangement as invented by Holborn and Kurlbaum[21] and independently by Morse[22] is shown in Fig. 17. In the common focal plane of the objective and eyepiece is placed a U-shaped lamp filament which is connected in series with a variable resistance, a battery, and a milliammeter. In front of the ocular is a filter of red glass which allows only a very narrow wavelength band, generally in the neighborhood of 6,300 Å (0.63 μ), to pass.

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[18] O. Lummer and E. Pringsheim, *Wied. Ann.*, **63**, 395 (1897), *et seq.*

[19] W. Nernst and T. Wulf, *Ber. deut. phys. Ges.*, **21**, 294 (1919); H. Rubens and G. Michel, *Verh. preus. Akad.*, **38**, 590 (1921).

[20] H. Le Chatelier, *Compt. rend.*, **114**, 214 (1892); *Jour. Phys.*, [3], **1**, 185 (1892).

[21] L. Holborn and F. Kurlbaum, *Ann. Phys.*, **10**, 225 (1902).

[22] E. F. Morse, *Am. Machinist*, **26**, 1514 (1903).

In operation, the pyrometer is focused upon the source of high temperature, and one then sees the lamp filament superimposed upon the image of the source, as a background. The current through the lamp filament is now adjusted until the filament becomes indistinguishable from its surroundings. The current through the filament in this condition serves as an indication of the temperature of the source. In the later forms of this instrument made by the Leeds and Northrup Co., the current is determined by the use of a potentiometer.

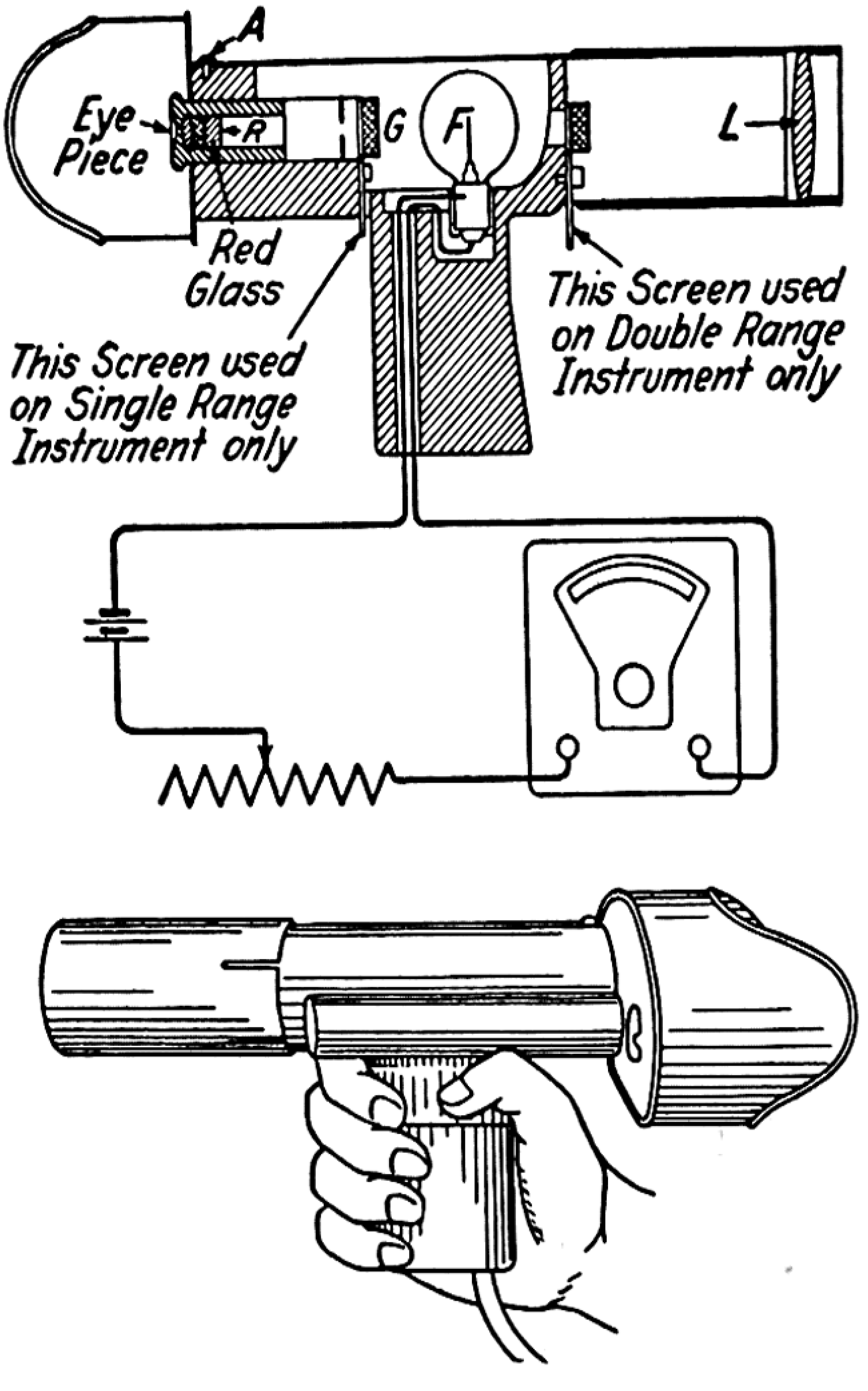
A
Eye Piece
R
G
F
L
Red Glass
This Screen used on Single Range Instrument only
This Screen used on Double Range Instrument only

FIG. 17. Optical pyrometer with disappearing filament.

Many other forms[23] of pyrometers, differing in the method of obtaining an adjustment between the radiation from the unknown source and that from a standard source, have been devised.

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[23] H. Wanner, *Wied. Ann.*, **53**, 785 (1894); C. Féry, *Jour. Phys.*, **3**, 32 (1904); W. E. Forsythe, "Temperature," *Amer. Inst. Phys.*, p. 115, *et seq.*, Reinhold Publishing Corporation, 1941.

Scale Law of the Optical Pyrometer with Disappearing Filament. It is apparent that the difference between the Wien and the Planck radiation laws is dependent upon the relative value of the expression $e^{C_2/\lambda T}$ and 1. In actual operation optical pyrometers employ absorbing glasses whose effective wavelength transmission λ has a value of about 0.63 micron. The value of C_2 is 14,320, so that at all ordinary temperatures $e^{C_2/\lambda T} \ggg 1$, and there is no practical difference between the two laws. Hence the simpler Wien law may be taken as the basis for the performance of optical pyrometers. An approximate scale law may be readily formulated if the following assumptions are allowed when the pyrometer is adjusted upon a radiating source at a temperature T.

(*a*) The equilibrium temperature of the filament (T_f) is proportional to the fourth root of the electrical power supplied to it ($r_f i^2$). This is merely the application of the Stefan-Boltzmann law to the radiation from the filament. r_f is the resistance of the filament and i is the current through it.

(*b*) The resistance of the filament r_f is proportional to its temperature (T_f).

(*c*) The Wien law applies to radiation from both the filament and the high-temperature source.

Then the milliammeter reading i may be expressed as

$$i = a\frac{T_f^2}{\sqrt{r_f}} = bT_f^{3/2} \tag{16}$$

When the filament is indistinguishable in the background, its emissive power is equal to the intensity of radiation in the same focal plane due to the source, so that

$$C_1\lambda^{-5}e^{-C_2/\lambda T_f} = C_1'\lambda^{-5}e^{-C_2/\lambda T} \tag{17}$$

Taking logarithms of each member in equation 17 gives

$$\frac{1}{T} = \frac{1}{T_f} + C = \frac{A}{i^{2/3}} + B \tag{18}$$

In these equations the quantities a, b, C, C_1, C_1', A, and B are constants whose magnitudes are of little interest.

It might thus be expected that, plotting $1/T$ against $1/i^{2/3}$, a straight-line relationship would result. In practice this is found to be true only over a very limited range in temperature. On this account it is not uncommon to express empirically the relationship between the current i and the temperature T as

$$T = a + bi + ci^2 + \cdots \qquad (19)$$

where the constants, a, b, c, etc., can be evaluated by calibrating at a corresponding number of known temperatures. It may be convenient to show the data graphically on a temperature-current coordinate plot.

Emissivity and Its Effect upon the Reading of an Optical Pyrometer. The emission from actual hot bodies is generally less in every wavelength than that from a black body at the same temperature. The result then follows that an optical pyrometer, calibrated by a black body, receives less energy than it should from the heated body and will indicate an apparent temperature T_A which is less than the true temperature T. A coefficient E_λ, called the characteristic emissivity may be defined as the ratio between the intensity of radiation at the wavelength λ from the actual body, to the intensity of radiation at the same wavelength from a black body at the same temperature. (See page 148.) Thus:

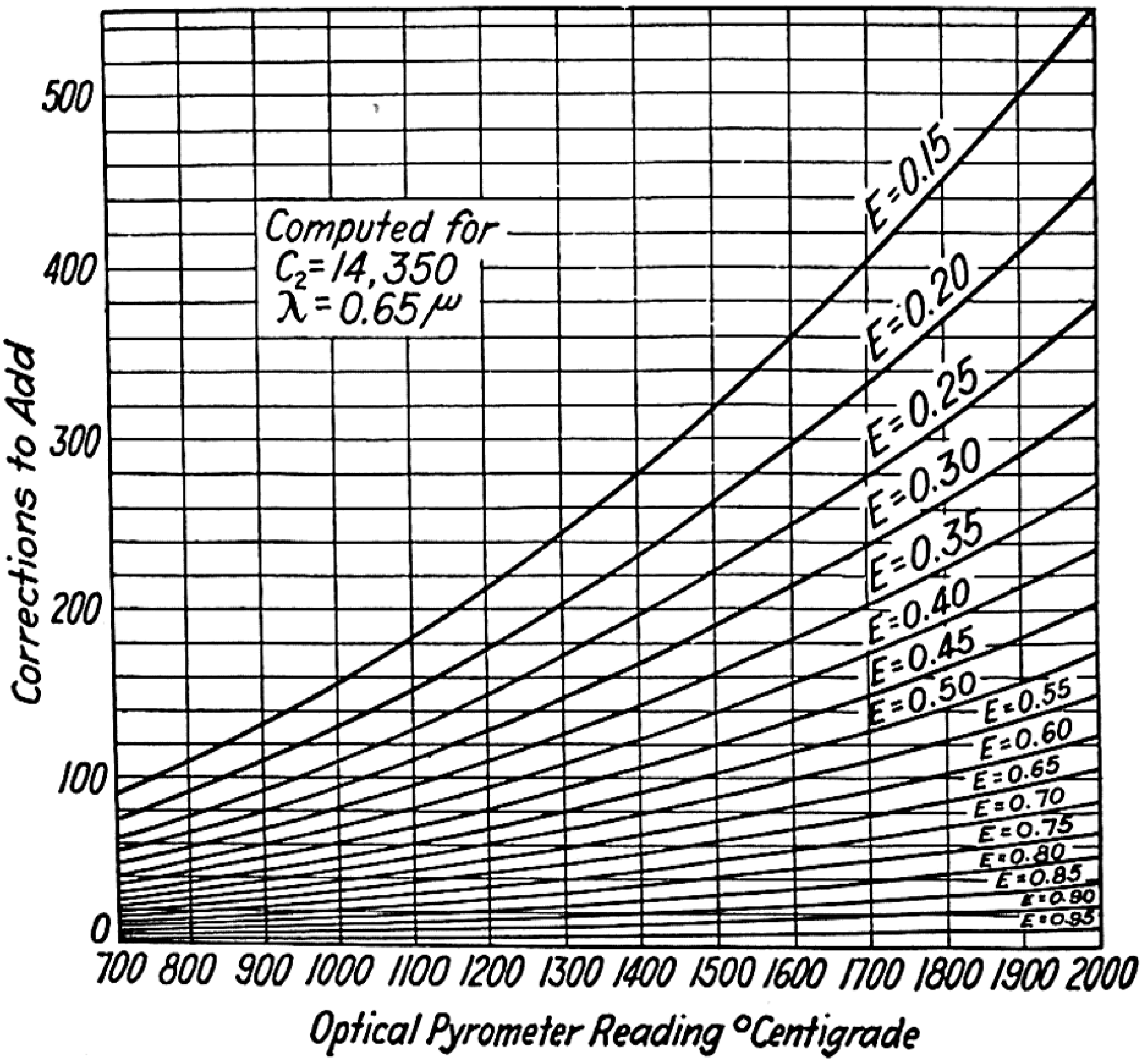

FIG. 18. Corrections due to reduced emissivity of the source (*Technologic Paper* 170, U. S. Bureau of Standards).

$$E_\lambda = \frac{J_\lambda \text{ (actual)}}{J_\lambda \text{ (black body)}} = \frac{C_1\lambda^{-5}e^{-C_2/\lambda T_A}}{C_1\lambda^{-5}e^{-C_2/\lambda T}} = e^{(C_2/\lambda)(1/T-1/T_A)} \qquad (20)$$

Taking logarithms of the first and last members in equation 20 and rearranging gives

$$\frac{1}{T} - \frac{1}{T_A} = \frac{\lambda}{C_2} \cdot \log_e E_\lambda = \frac{0.63(2.302)}{14{,}320} \log_{10} E_\lambda = \frac{\log_{10} E_\lambda}{9{,}874} \tag{21}$$

Thus it is only necessary to know any pair of true and apparent temperatures T and T_A to find E_λ or, conversely, if E_λ is known then any apparent temperature T_A may be corrected to the true value. The magnitude of these corrections computed for a wavelength of 0.65 micron and a value for C_2 of 14,350 is shown graphically in Fig. 18. The error in the measurement of a temperature when the emissivity of the source is small is not as great as might be expected. Thus for a body of emissivity $E_\lambda = 0.50$ an apparent temperature of 1,500° C. is in error by only about 100° C.

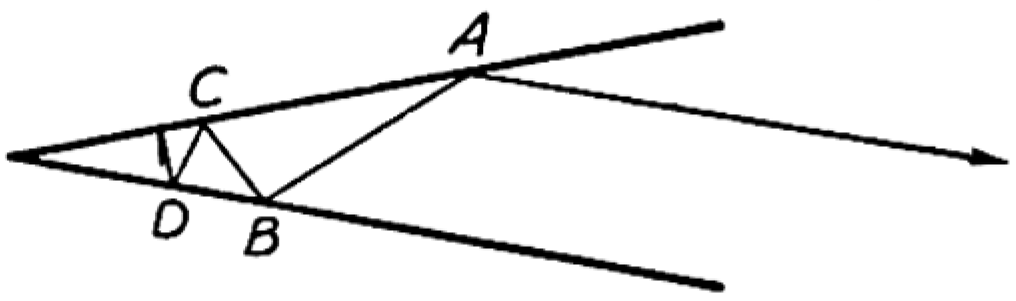

FIG. 19. The emission of radiation from a hollow wedge (Mendenhall).

Radiation from Cavities. Mendenhall[24] has shown that even for materials of very low emissivity black-body conditions may be approximated if the pyrometer is sighted upon the inside surface of a hollow wedge of the material, having a small angular opening. Thus in Fig. 19 the radiation going to the pyrometer from A is only in part emitted by the surface at A. In addition some radiation is included which originated at B and suffered reflection at A, while also some radiation is present from C after successive reflections at B and A; etc.

Thus the intensity of the emergent radiation is

$$I_\lambda = [E_\lambda + E_\lambda R_\lambda + E_\lambda R_\lambda^2 + \cdots] J_\lambda \tag{22}$$

where J_λ is the monochromatic intensity of radiation from a black body at the same temperature, E_λ is the actual emissivity of the surface, and R_λ is the reflectivity of the same surface for the same wavelength. The law of Kirchhoff (see page 151) states that for any material:

$$E_\lambda + R_\lambda = 1 \tag{23}$$

i.e., a good reflector is a correspondingly poor emitter of radiation of the same wavelength). Hence equation 22 may be transformed by substitution so that all terms in the bracket but the first and last annul each other, giving

$$I_\lambda = [1 - R_\lambda + R_\lambda - R_\lambda^2 + R_\lambda^2 \cdots - R^n] [J_\lambda] \doteq J_{\lambda\,\text{(black body)}} \tag{24}$$

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[24] C. E. Mendenhall, *Phys. Rev.*, **33**, 74 (1911). See also paper by A. G. Worthing, *Phys. Rev.*, **25**, 846 (1925).

In actual practice, if as many as ten reflections are allowed, the term R^n becomes negligible and the radiation is sensibly black-body radiation. Rough oxide-coated surfaces approximate this condition.

Absorbing Materials and the Extension of the Range of Pyrometers. When radiation of intensity I passes into a layer of material of thickness dx, the intensity is reduced by a quantity dI. The quantity dI is proportional both to I and dx as well as to the absorbing property μ of the material of the layer. This quantity μ may be defined in units such that

$$dI = \mu I dx \tag{25}$$

By the integration of this equation for a finite layer of thickness t and an incident beam of intensity I_0, the intensity of the emergent beam I is

$$I = I_0 e^{-\mu t} \tag{26}$$

The absorption coefficient of the material μ is thus numerically the reciprocal of that thickness which would reduce the emergent intensity I to $1/e$ of its incident value I_0. Hence if such an absorbing screen is placed between a pyrometer and a source of high temperature, then the pyrometer receives only the fraction $I/I_0 = e^{-\mu t}$ of the radiation it would have received with no obstruction. The apparent temperature of the body then will be less than its true temperature. It is evident that $e^{-\mu t}$ plays the role of E_λ in equation 21, and therefore:

$$\frac{1}{T} - \frac{1}{T_A} = \frac{-\mu t \lambda}{C_2} \tag{27}$$

This enables the range of the pyrometer to be extended beyond its normal calibrated values. The right-hand member is a constant which may be evaluated by any pair of true and apparent temperatures. Then any other apparent temperature T_A may be converted to its corresponding true value T.

The range of optical pyrometers may also be extended by rotating between the source and the pyrometer a slotted disk whose ratio of open space to total space is the proper fraction R. With the disk spinning in place, only a fraction R of the total radiation expected will be received by the pyrometer. The apparent temperature T_A will be less than the true temperature T. The value R evidently again plays the part of E_λ in equation 21, so that

$$\frac{1}{T} - \frac{1}{T_A} = \frac{\log_{10} R}{9{,}874} \tag{28}$$

The quantity R may be measured independently by a protractor. If it be made sufficiently small, the upper limit of temperature, measurable by the pyrometer, may be made indefinitely high.

A Two-Color Optical Pyrometer. Even though the emissivity of a surface is small and unknown it may still be possible to measure the temperature correctly by the method of the optical pyrometer. One method recently described[25] assumes that the emissivity although unknown is the same at two different wavelengths λ_1 and λ_2. Such a body is often termed a "gray" body. Equation 23 for the intensity of radiation may be written for the two wavelengths, giving

$$J_{\lambda_1} = C_1 E_{\lambda_1} \lambda_1^{-5} e^{-C_2/\lambda_1 T} \tag{29}$$

and

$$J_{\lambda_2} = C_1 E_{\lambda_2} \lambda_2^{-5} e^{-C_2/\lambda_2 T} \tag{30}$$

By forming the ratio of these equations and then taking the logarithm of the ratio, it follows that

$$\log \frac{J_{\lambda_1}}{J_{\lambda_2}} = A + \frac{B}{T} \tag{31}$$

It is thus apparent that if the ratio of the intensities at the two wavelengths can be determined then the temperature can be evaluated.

To accomplish this, light from the source is passed through an objective lens onto the surface of an inclined semitransparent gold mirror. The transmitted light passes through a green filter on to its detector while the reflected beam passes through a red filter to its detector. Properly adjusted photoelectric cells may be used as detectors with their output currents amplified by vacuum tube circuits, and balanced by a Wheatstone bridge network. The constants A and B could be calculated if the wavelengths were known exactly, or they could be determined by calibrating the apparatus at two known temperatures.

TOTAL RADIATION PYROMETERS

The Stefan-Boltzmann Law. From experiments made by J. Tyndall and by P. L. Dulong and A. T. Petit on the rate at which hot bodies cooled, J. Stefan[26] concluded that the radiation from the surface was proportional to the fourth power of the absolute temperature of the body. A similar result was deduced theoretically by L. Boltzmann[27] a few years later. Since the radiating body would also be receiving heat proportional to the fourth power of the temperature of its surroundings, the net loss in energy per square centimeter per second is given by the following:

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[25] H. W. Russell, C. F. Lucks, and L. G. Turnbull, "Temperature," Amer. Inst. Phys., p. 1159, Reinhold Publishing Corporation, 1941.

[26] J. Stefan, *Wien. Ber.*, **79** A, 2, 391 (1879).

[27] L. Boltzmann *Wied. Annal.*, **26**, 287 (1884).

$$W = \sigma(T^4 - T_0^4) \tag{32}$$

where σ is a universal constant 5.672×10^{-12} when W is expressed in joules and T and T_0 are the temperatures of the radiating body and its surroundings, respectively, on the absolute scale.

The Féry Total Radiation Pyrometer. Having established a relationship between the total radiation from the surface of a body and its temperature, a measurement of the radiation would be sufficient to determine the temperature. One of the first devices whose operation was based upon this law was proposed by C. Féry[28] in 1902. This device is shown in Fig. 20. Although this pyrometer is not now used extensively, it illustrates the principle of all such instruments. The radiation entering the opening of the cylindrical tube is focused by the concave mirror upon a small thermocouple at D. The thermojunction is connected through binding posts B to a suspension galvanometer. As an aid in focusing, two inclined mirrors, together with an eyepiece, are arranged so that when properly focused the field of view appears as a complete disk and in all other positions the two half disks are displaced with respect to each other.

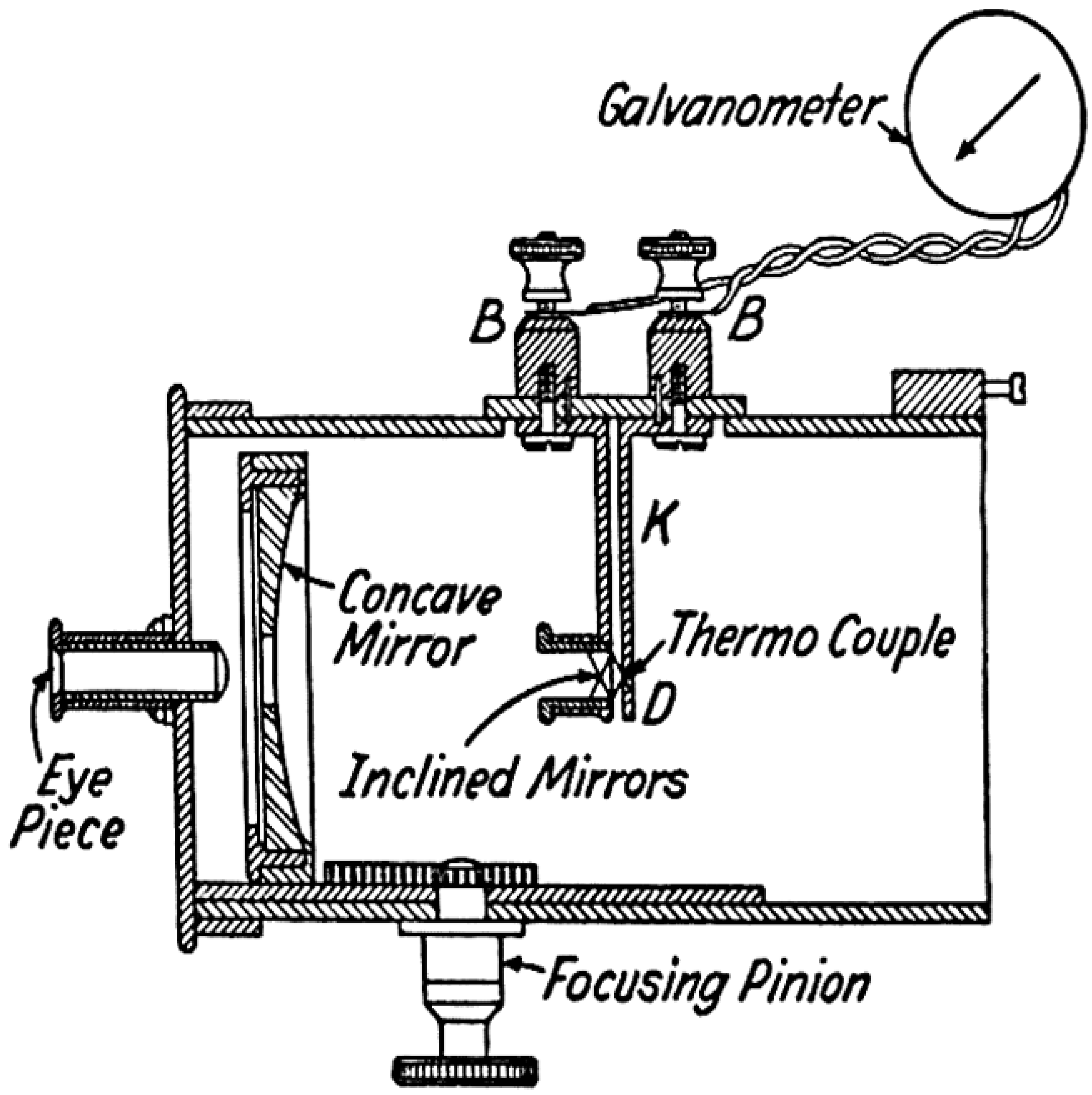

FIG. 20. The Féry total radiation pyrometer.

Other total radiation pyrometers have been described. These differ in general only by the method in which the radiation received is brought to a focus upon the thermojunction. Thus in the Thwing instrument, the thermoelement is at the apex of a conical mirror.

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[28] C. Féry, *Compt. rend.*, **134**, 997 (1902).

Most frequently the radiation is focused by reflections from the front faces of mirrors. This is necessary since the radiation from bodies at temperatures not too high is, for the most part, in the infrared spectral region and would be quite completely absorbed by transmission through glass sheets or lenses. Lenses of fluorite have been employed with some success, but as they are so readily damaged their use is not common.

A radiation pyrometer capable of indicating temperatures between −100° C. and +100° C. with an accuracy of 0.1° C. has been described by J. Strong.[29] This pyrometer makes use of the characteristic reflection of radiation of certain definite wavelengths from crystalline surfaces. Using 5 successive reflections from quartz only narrow wavelength bands at 9 and 19 microns are transmitted. These wavelengths are not reflected by ordinary surfaces, hence the temperature of a body may be observed regardless of any other illumination incident upon it.

Scale Law for Radiation Pyrometers. The relationship to be expected between the deflection of the indicating instrument and the temperature of the source may be predicted approximately. The following assumptions are made:

(*a*) The deflection D of the galvanometer is proportional to the emf. applied to it.

(*b*) The emf. — temperature relationship of the thermocouple in the pyrometer is linear. Then D will vary as the difference in temperature between the hot and cold junctions of the thermocouple $(T_2' - T_1')$.

(*c*) Newton's law of cooling is applicable to the equilibrium temperature of the thermocouple. That is, the increase in temperature of the junction of the couple above the surrounding temperature $(T_2' - T_1')$ is proportional to the rate of receiving heat which by the Stefan law is proportional to $(T^4 - T_0^4)$ where T is the temperature of the source and T_0 is that of its surroundings.

Then the deflection

$$D \propto \text{emf.} \propto (T_2' - T_1')_{\text{couple}} \propto (T^4 - T_0^4) \tag{33}$$

so that

$$D = aT^4 + b \tag{34}$$

where a and b are constants. If T_0 is small compared to T then b may be neglected, and by forming the logarithm of each member it follows that

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[29] J. Strong, *Rev. Sci. Inst.*, **29**, 520 (1939).

$$\log D = A + 4 \log T \tag{35}$$

where A is written for the constant $\log a$. Thus on a $\log T$ versus $\log D$ coordinate system a straight line whose slope is 4 should represent the calibration of a radiation pyrometer. This is found to be almost exactly the case in practice, so that a calibration at two points gives a complete calibration of the instrument.

The Effect of Varying the Distance to the Source upon the Reading of a Pyrometer. In the absence of absorbing media the readings of a radiation pyrometer may be independent of the distance of the source from the pyrometer. This may be illustrated by reference to Fig. 20, but it is equally true for optical pyrometers. If the source be removed to a distance twice as far away, then approximately one-fourth as much energy is received by the mirror. This radiation is focused upon the surface containing the thermojunction, forming an image whose area is approximately one-fourth that of the original image. Hence the energy per square millimeter in the image on the thermojunction is constant. In order that the indication of the instrument be independent of distance it then is necessary that the diameter of the image of the source always be greater than that of the receiving disk of the thermojunction.

THE MEASUREMENT OF TEMPERATURE BY THE OBSERVATION OF THE WAVELENGTH OF MAXIMUM ENERGY

At the peak of the curves in Fig. 16 (i.e., position of maximum intensity of radiation), the slope of the curve ($dJ_\lambda/d\lambda$) is zero. The differentiation of equations 14 or 15 with respect to λ yields an expression which when set equal to zero results in the following very simple relationship.

$$\lambda_{(\text{max. energy})}\, T = \frac{C_2}{5} = C \tag{36}$$

The value of the product $\lambda_{(\text{max. energy})} T$ best fitting the results of Lummer and Pringsheim was 2,990 when λ was in microns and T in degrees absolute. More recent experimental values indicate for this constant the value 2,897.1. This relationship allows therefore the determination of the temperature of very remote sources, such as stars. It is only necessary to determine the wavelength of greatest intensity in the spectrum of the star. Then the absolute temperature is given by

$$T = \frac{2{,}897.1}{\lambda_{(\text{max. energy})}} \tag{37}$$

This does not demand an absolute measure of the intensity of radiation.

Still another method making use of the laws of radiation may be devised for the measurement of temperature. Equation 62 in Chapter V shows that, if the intensities of radiation for the positions of maximum energy for any two sources can be compared, then the ratio of these intensities is also the ratio of the fifth power of the absolute temperatures of the two sources. So that

$$\left(\frac{J_\lambda}{J'_\lambda}\right)_{(\text{max. energy})} = \left(\frac{T}{T'}\right)^5 \tag{38}$$

THE INTERNATIONAL SCALE OF TEMPERATURE

In 1887 the International Committee on Weights and Measures, recognizing the need for a standard scale of temperature, adopted the following resolution:

> "The International Committee on Weights and Measures adopts as the standard thermometric scale for the international service of weights and measures, the centigrade scale of the hydrogen thermometer, having as fixed points the temperature of melting ice (0° C.) and of the vapor of distilled water boiling at standard atmospheric pressure (100° C.); the hydrogen being at an initial manometric pressure of one meter of mercury."

Various national physical laboratories employed the constant-volume gas thermometer to determine the freezing points and the boiling points of many pure substances. For work at high temperatures nitrogen was substituted for hydrogen, since most materials are then not impervious to the passage of hydrogen. For very low temperatures helium is used, since it remains a gas at temperatures below that at which the hydrogen has liquefied. In using these modifications of the normal thermometer, corrections could be applied to adjust the observed temperatures to the hydrogen scale. However, since hydrogen itself differs from an ideal gas, it seemed more rational to correct the observed temperatures to an ideal gas or Kelvin scale. By 1920 most national laboratories had abandoned the international hydrogen scale as an ultimate standard.

Acting first at the Seventh General Conference on Weights and Measures in 1927 and again in 1933 the representatives of thirty-one nations unanimously adopted a new international temperature scale. The definition of this scale as adopted follows:

1. The thermodynamic centigrade scale, on which the temperature of melting ice, and the temperature of condensing water vapor, both under the pressure of one standard atmosphere, are numbered 0° and

100°, respectively, was recognized as the fundamental scale to which all temperature measurements should ultimately be referable.

2. The experimental difficulties incident to the practical realization of the thermodynamic scale made it expedient to adopt for international use a practical scale designated as the " International Temperature Scale." This scale conforms with the thermodynamic scale as closely as is possible with present knowledge, and is designed to be definite, conveniently and accurately reproducible, and to provide means for uniquely determining any temperature within the range of the scale, thus promoting uniformity in numerical statements of temperature.

3. Temperatures on the international scale are to be designated as " °C," but may be designated as " °C (Int.)" if it is desired to emphasize the fact that this scale is being used.

4. The International Temperature Scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated according to a specified procedure at the fixed temperatures.

5. The basic fixed points and the numerical values assigned to them for the pressure of one standard atmosphere are given in the following table, together with the formulae which represent the temperature (T_p) as a function of the vapor pressure (p) over the range 680 to 780 mm. of mercury.

6. Basic fixed points of the International Temperature Scale:

a. Temperature of equilibrium between liquid and gaseous oxygen −182.97° C.

$$T_p = T_{760} + 0.0126(p - 760) - 0.0000065(p - 760)^2 \qquad (39)$$

b. Temperature of equilibrium between ice and air-saturated water 0.00° C.

c. Temperature of equilibrium between liquid water and its vapor 100.000° C.

$$T_p = T_{760} + 0.0367(p - 760) - 0.000023(p - 760)^2 \qquad (40)$$

d. Temperature of equilibrium between liquid sulphur and its vapor 444.60° C.

$$T_p = T_{760} + 0.0909(p - 760) - 0.000048(p - 760)^2 \qquad (41)$$

e. Temperature of equilibrium between solid silver and liquid silver 960.5° C.

f. Temperature of equilibrium between solid gold and liquid gold 1063.0° C.

Standard atmospheric pressure was defined as the pressure due to a column of mercury 760 mm. high, having a density of 13.5951 gm./cm.^{3}, subject to a gravitational acceleration of 980.665 cm./sec.^{2} and is equal to 1,013,250 dynes/cm.^{2}.

It is an essential feature of a practical scale of temperature that definite numerical values shall be assigned to such fixed points as are chosen. It should be noted, however, that the last decimal place given for each of the values in the table is significant only as regards the degree of reproducibility of that fixed point on the International Temperature Scale. It is not to be understood that the values are necessarily known on the thermodynamic centigrade scale to the corresponding degree of accuracy.

7. The means available for interpolation lead to a division of the scale into four parts.

a. From the ice point to 660° C. the temperature T is deduced from the resistance R_T of a standard platinum resistance thermometer by means of the formula.

$$R_T = R_0(1 + AT + BT^2) \tag{42}$$

The constants R_0, A, and B of this formula are to be determined by calibration at the ice, steam, and sulphur points, respectively.

The purity and physical condition of the platinum of which the thermometer is made should be such that the ratio R_T/R_0 shall not be less than 1.390 for T equal 100° and 2.645 for T equal 444.6°.

b. From $-190°$ C. to the ice point, the temperature T is deduced from the resistance R_T of a standard platinum resistance thermometer by means of the formula

$$R_T = R_0[1 + AT + BT^2 + C(T - 100)T^3] \tag{43}$$

The constants R_0, A, and B are to be determined as specified above, and the additional constant C is determined by calibration at the oxygen point. The standard thermometer for use below 0° C. must, in addition, have a ratio R_T/R_0 less than 0.250 for T equal to $-183°$ C.

c. From 660° C. to the gold point, the temperature T is deduced from the electromotive force e of a standard platinum versus platinum-rhodium thermojunction, one junction of which is kept at a constant temperature of 0° C. while the other is at the temperature T defined by the formula

$$e = a + bT + cT^2$$

The constants a, b, and c are to be determined by calibration at the freezing point of antimony and at the silver and gold points.

d. Above the gold point the temperature T is determined by means of the ratio of the intensity J_2 of monochromatic visible radiation of wavelength 0.000063*cm*, emitted by a black body at the temperature T_2, to the intensity J_1 of radiation of the same wavelength emitted by a black body at the gold point, by means of the formula

$$\log_e \frac{J_2}{J_1} = \frac{C_2}{\lambda}\left[\frac{1}{1{,}336} - \frac{1}{T + 273}\right] \tag{44}$$

The constant C_2 is taken as 1.432*cm* degrees. The equation is valid if $\lambda(T + 273)$ is less than 0.3*cm* degrees.

At subsequent meetings of the International Committee it is expected that certain minor revisions will be proposed for the scale. Typical of such suggestions are the extension of the scale below −190° C., the use of a slightly higher value for the constant C_2 and the substitution of the Planck formula for the Wien radiation law.

The devices used for measuring temperature over the various ranges and the accepted values of certain fixed temperatures are shown in Fig. 21.

The Measurement of Very Low Temperatures. Although no provision is made in the international scale for temperatures below −190° C. this range cannot be regarded as unimportant. In addition to the vapor pressure thermometers already described, resistance thermometers, thermocouples, and a measure of magnetic susceptibility may serve to indicate temperature over certain parts of this range.

For very low temperatures the standard platinum resistance thermometer lacks sensitivity. The most satisfactory metals are alloys such as phosphor-bronze containing a trace of lead. A particular sample of this has been described[30] in which the resistance decreases linearly as the temperature is varied from 7° K. to 0.04° K. Unlike the metals, the resistance of carbon increases rapidly as it is cooled toward the absolute zero. This material has been used[31] with some success at temperatures down to 0.2° K. Since the resistance may be greatly altered by the presence of a magnetic field or even by the measuring current, these resistance devices must be used with care. The relative change in resistance for these two materials with temperature is shown in Fig. 22. The ordinate shows the ratio of the resistance of the specimen R_T at any temperature T, to the resistance R_6 at the temperature 6° K.

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[30] J. F. Allen and E. S. Shire, *Nature*, **139**, 878 (1937).

[31] W. F. Giauque, J. W. Stout, and C. W. Clark, *Jour. Amer. Chem. Soc.*, **60**, 1053 (1938).

Thermocouples of copper versus constantan may be used down to very low temperatures with a decreasing sensitivity. A thermocouple usable to 2° K. with a large and uniform temperature coefficient has

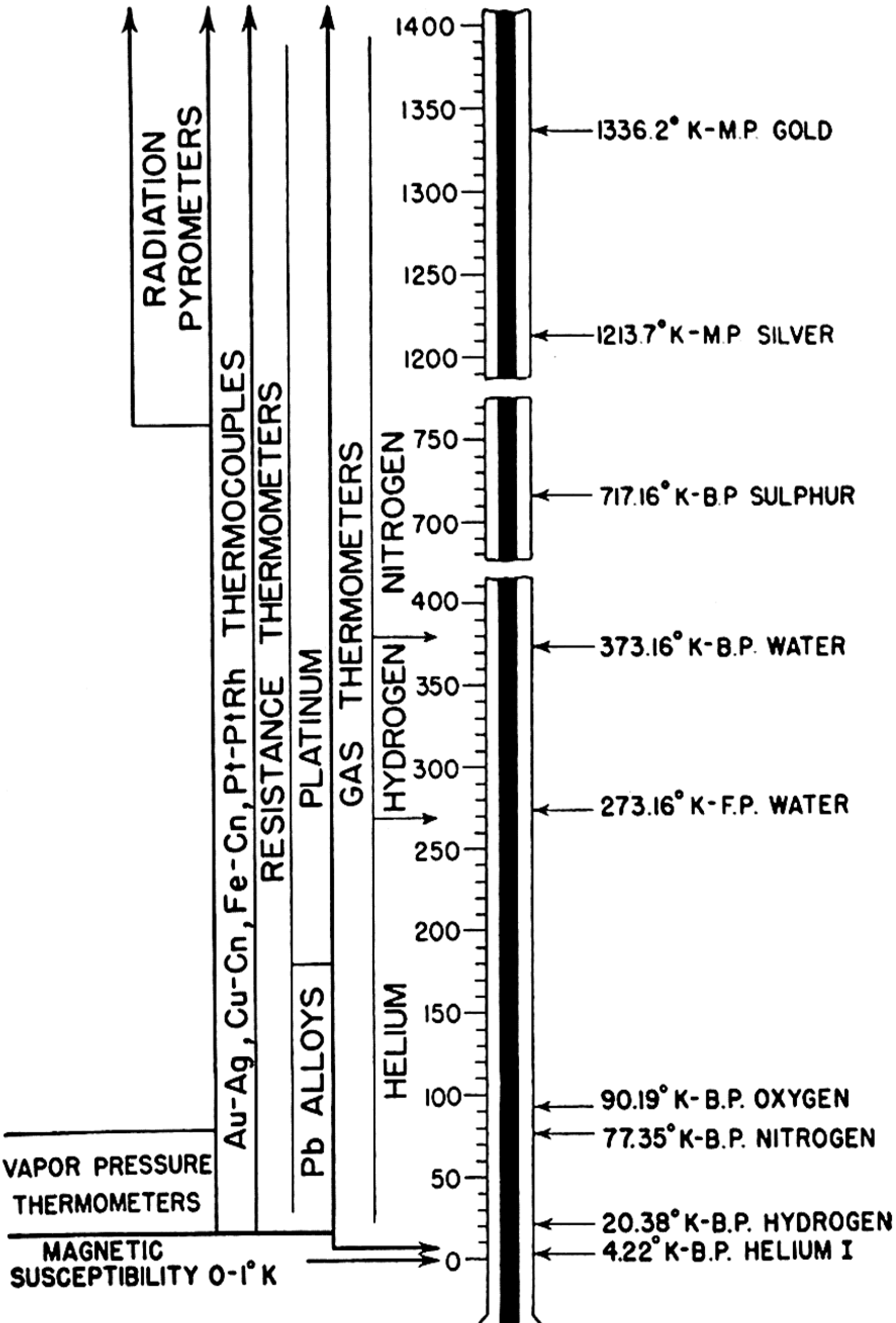

FIG. 21. Fixed temperatures and useful ranges for various temperature-measuring devices.

been described by Keesom and Matthijs.[32] The metals consist of an alloy of gold (gold 98%, cobalt 2%) versus a standard alloy of silver (silver 99.63%, copper 0.37%).

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[32] W. H. Keesom and C. F. Matthijs, *Physica*, **2**, 623 (1935).

The very lowest temperatures have been produced by the adiabatic demagnetization of certain paramagnetic substances, as will be described later. The temperature attained has been estimated[33] by measuring the magnetic susceptibility of the specimen and assuming that the susceptibility varies inversely with the absolute temperature. This resolves itself into a very sensitive weighing operation.

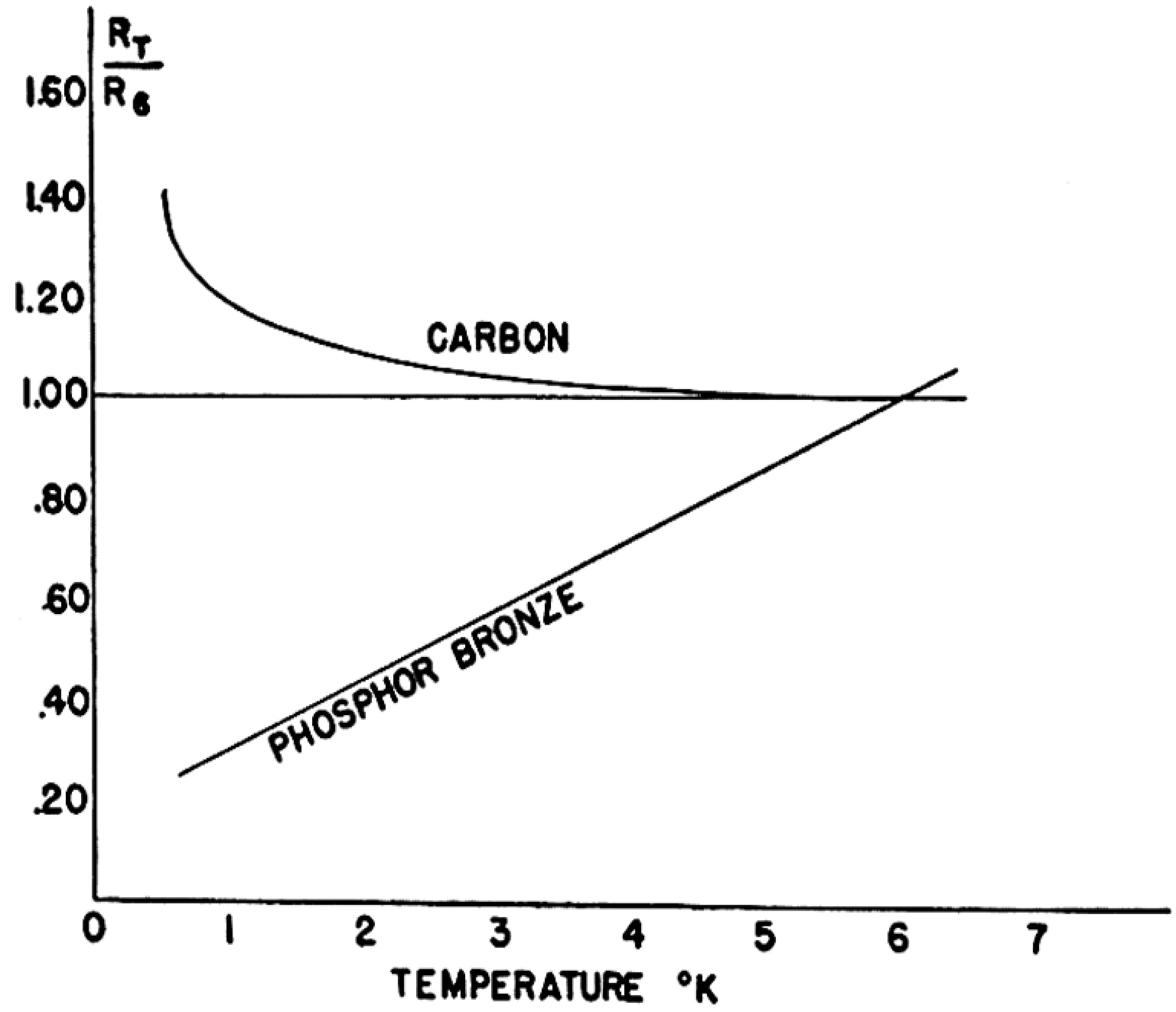

FIG. 22. Relative resistivities of carbon and phosphor bronze at very low temperatures.

QUESTIONS AND PROBLEMS

1. A noble-metal thermocouple has its cold junction at a temperature of 40° C., and when connected to a potentiometer calibrated in degrees for cold junction at 0° C., a reading of 800° C. is observed. What is the true temperature of the hot junction? Construct an empirical formula for the true temperature. See Appendix for tables.

2. A certain resistance thermometer is observed to have the following resistances: 11.00 ohms in melting ice, 15.247 ohms above boiling water at 760 mm. pressure, and 28.887 ohms above boiling sulphur at 760 mm. pressure (444.55° C.). Express the values of α and β in an empirical resistance-temperature equation. What is the value of δ in the Callendar correction formula?

3. From the result of problem 2, what would be the observed platinum temperature with this thermometer when immersed in melting tin (232° C.).

4. Calculate the relative increase in the intensity of radiation at 0.5μ as the temperature of the source changes from 500° C. to 1,000° C. Do the same at a wavelength of 2μ. What phenomenon does this explain?

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[33] W. J. DeHaas and E. C. Wiersma, *Physica*, **2**, 235 (1935).

5. An optical pyrometer sighted upon the inside of a hollow metallic wedge indicates a temperature of 1,200° C., whereas when focused upon the outside the apparent temperature is 1,160° C. What is the emissivity of the material of the wedge?

6. It is desired to observe the temperature of the sun (5,800° C.) on a pyrometer so that its apparent temperature is 2,000° C. By using an interposed rotating disk what should be the total angular opening of the slots to permit this?

7. The true temperature of a certain source is 950° C. and when viewed through a certain absorbing glass of thickness 4 mm. the apparent temperature is 890° C. What is the absorption coefficient of the absorbing material for the radiation of the wavelength employed by the pyrometer ($\lambda = 0.63\mu$)?

8. A radiation pyrometer when sighted upon a molten metal surface indicates a temperature of 900° C. while a thermocouple indicates a temperature of 960° C. If there is no error in the instrument what is the total emissivity of the surface?

9. In photographing the spectrum of a star, maximum blackening is found to occur upon the photographic plate in the ultraviolet region at 2,300 Å. Assuming the emulsion of the photographic plate to be equally sensitive to all wavelengths, what is the approximate temperature of the star?

10. A mercury-in-glass thermometer has a spherical bulb 1 cm. in diameter. The cylindrical capillary has an internal diameter of 0.2 mm. What is the length of the temperature scale for 1 deg.? Assume the volumetric coefficient for glass and mercury to be 0.000024 and 0.000182 deg. $C.^{-1}$, respectively.

11. In a constant-volume gas thermometer the pressures observed at the freezing and boiling points of pure water are 1,000 and 1,364.2 mm. of mercury, respectively. The barometer reads 746 mm. The thermometer bulb is made of glass. What does this indicate for the temperature at the absolute zero?

12. Show that if a centigrade, a Fahrenheit, and a Réaumur thermometer are exposed to the same temperature, the reading of the Fahrenheit thermometer is the sum of the readings of the other thermometers plus 32.

CHAPTER II

SPECIFIC HEATS

Nature of Heat. Until the beginning of the nineteenth century the view most commonly held regarding the nature of heat was that it was a material substance, exceedingly light, and very elastic. By assuming that the particles of this substance (called caloric) were highly self-repellent, the emission of light and radiant energy were explained. It was further postulated that although the particles of caloric were mutually self-repellent they were very strongly attracted by the particles of ordinary matter. The force exerted by any one substance upon caloric was regarded as variable if the substance were treated in certain ways, such as being struck or bent. It was assumed that the ability of the matter to hold caloric was diminished by this treatment so that some caloric was ejected; similarly the development of heat by friction could be explained.

That heat was not a material substance of this nature but that its presence in a body was related to the motion of the particles of that body was perhaps first intimated by Lord Bacon.[1] The conclusions of Bacon were based upon philosophic reasoning rather than experimental facts. Exact definite experimental evidence casting a doubt upon the existence of caloric as a material substance appeared for the first time in 1798. A paper by Count Rumford[2] entitled " An Inquiry Concerning the Source of Heat Which is Excited by Friction " was presented to the Royal Society of London at that time. In directing the arsenal at Munich, Rumford had been impressed by the large amount of heat that was developed continuously in the process of drilling a cannon. He proceeded to carry out an experiment in which a blunt drill driven by horses was made to work against the casting from which a brass six-pounder was made. Measurements were made of the horse-hours of work input and of the heat developed in the drill, metal chips, and cannon by placing them in contact with water. One sees here the peculiar property that must be ascribed to caloric if its existence is allowed, namely, the more of this material that is abstracted in the process of drilling, the more of the same substance seems to remain in the cannon being drilled. Rumford concluded " . . . it appears to me to be extremely difficult if not impossible to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments, except it be motion."

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[1] See *Novum Organum*, Liber II, Aph. 16.

[2] Benjamin, Count of Rumford (born Benjamin Thomson, Woburn, Mass., 1753), *Roy. Soc. Phil. Trans.* (*London*), **88**, 80 (1798).

Another experimental result on a similar subject was reported by Rumford[3] in the same year. He had attempted with the most sensitive balance available to detect changes in the weight of a body as its temperature was changed. He concluded that " All attempts to discover any effect of heat upon the apparent weights of bodies will be fruitless."

A more crucial experiment was reported in 1799 by Sir Humphry Davy.[4] It was admitted by the calorists that the total heat content of a mass of water was greater than that of an equal mass of ice, as the ice in melting was known to absorb a large quantity of heat with no accompanying change in temperature. Davy started with two pieces of ice at 29° F. in an atmosphere at the same temperature. Rubbing them together with a vigorous motion for a few minutes enabled him to collect a certain mass of water at a temperature of 35° F. and to observe the disappearance of an equivalent mass of ice. The heat required to effect this transformation could conceivably have its origin nowhere except in the motion. Davy concluded " Heat . . . may be . . . probably a vibration of the corpuscles of bodies tending to separate them."

Despite the soundness of these experiments, the doctrine of caloric was so firmly intrenched that it was almost fifty years before it was replaced by the more plausible " kinetic theory " of heat. The equivalence between heat and mechanical energy was proposed in 1842 by Dr. J. R. Mayer[5] from philosophic reasoning. The first experimental exposition of the relationship was reported in 1843 by J. P. Joule.[6] Although unrecognized by other scientists at the time, Joule persisted in his researches and reported again to the British Association in 1847. The reception accorded the announcement of the law of the conservation of energy as applied to thermal processes by Joule in 1847 marked the end of popular acceptance of the caloric theory.

Kinetic Model. Each of the many phenomena observed in the field of heat was found to support admirably the doctrine that heat is a form of energy, resident in the random motions of the particles of which a body is composed. In gases the particles are assumed to travel between collisions with approximately uniform motion. In liquids, also, uniform motion characterizes the particle until it approaches close to the free surface. In solids a definite particle is associated with a particular point on a three-dimensional lattice, and although it may undergo vibratory motion about this point as a center it cannot migrate to another part of the lattice until the melting point is exceeded.

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[3] Benjamin, Count of Rumford, *Roy. Soc. Phil. Trans. (London)*, **89**, 179 (1798).

[4] Sir Humphry Davy, " Essay on Heat and Light," Complete Works, Vol. 2, p. 11.

[5] J. R. Mayer, *Liebig's Annalen*, **42**, 233 (1842).

[6] J. P. Joule, *Phil. Mag.*, [3], **23**, 355, 439 (1843).

In a gas whose molecules are " mass points " (i.e., monatomic and of negligible volume), only translational energy may exist in the particles. Since such movement is possible in three mutually perpendicular directions, this motion is considered to be characterized by three degrees of freedom. Now, if the gas molecules are polyatomic, certain additional ways of storing energy are possible. These may consist in a vibration of the component atoms of the molecule relative to each other, or a rotation of the molecule about those axes for which the moments of inertia of the molecule as a whole are not too small. These motions introduce additional degrees of freedom. In the solid state, in addition to these modes of storing energy, vibrations of the molecule as a whole, with respect to the lattice, are possible.

The Principle of the Equipartition of Energy. In the classical consideration of the problem of the distribution of energy among the various degrees of freedom a postulate known as the " equipartition principle " has been allowed. According to this principle, if heat is added to a body it automatically divides so that each degree of freedom statistically shares equally in the increase. Although in the quantum theory this principle will not be retained it has been very helpful in the development of the subject.

Definitions. The term quantity of heat, introduced before the ultimate nature of heat was recognized, loses none of its significance, whatever theory be accepted. By definition, heat was that something which if present in a body in larger quantity (provided no change in state was allowed) resulted in a higher temperature in the body. Thus to set up a unit for measuring heat one need only agree upon the amount and kind of substance to be heated and the elevation in temperature to be associated with a unit quantity. By referring to the results of Rowland,[7] Bousfield,[8] Callendar,[9] and others, it is observed that for a definite amount of water the quantities of heat needed to produce equal successive elevations of temperature are somewhat different, depending upon the temperature of the water. This relationship, as averaged from the results of several observers, is illustrated in Fig. 23. A minimum value in the quantity of heat necessary to be added to produce an elevation in temperature of 1 deg. is variously reported as occurring at temperatures from 25° C. up to 40° C. It would logically appear that choosing 1 gm. of water as the receiving body then one one-hundredth part of that quantity of heat that would raise the temperature from 0° C. to 100° C. might well be chosen as the fundamental unit of quantity of heat. This was originally thought to be also the quantity of heat

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[7] H. A. Rowland, *Proc. Amer. Acad. Sci.*, **15**, 75 (1879).

[8] W. R. Bousfield, *Proc. Roy. Soc. (London)*, **93**, 587 (1917).

[9] H. L. Callendar, *Phil. Trans. Roy. Soc. (London)*, **212**, 1 (1912).

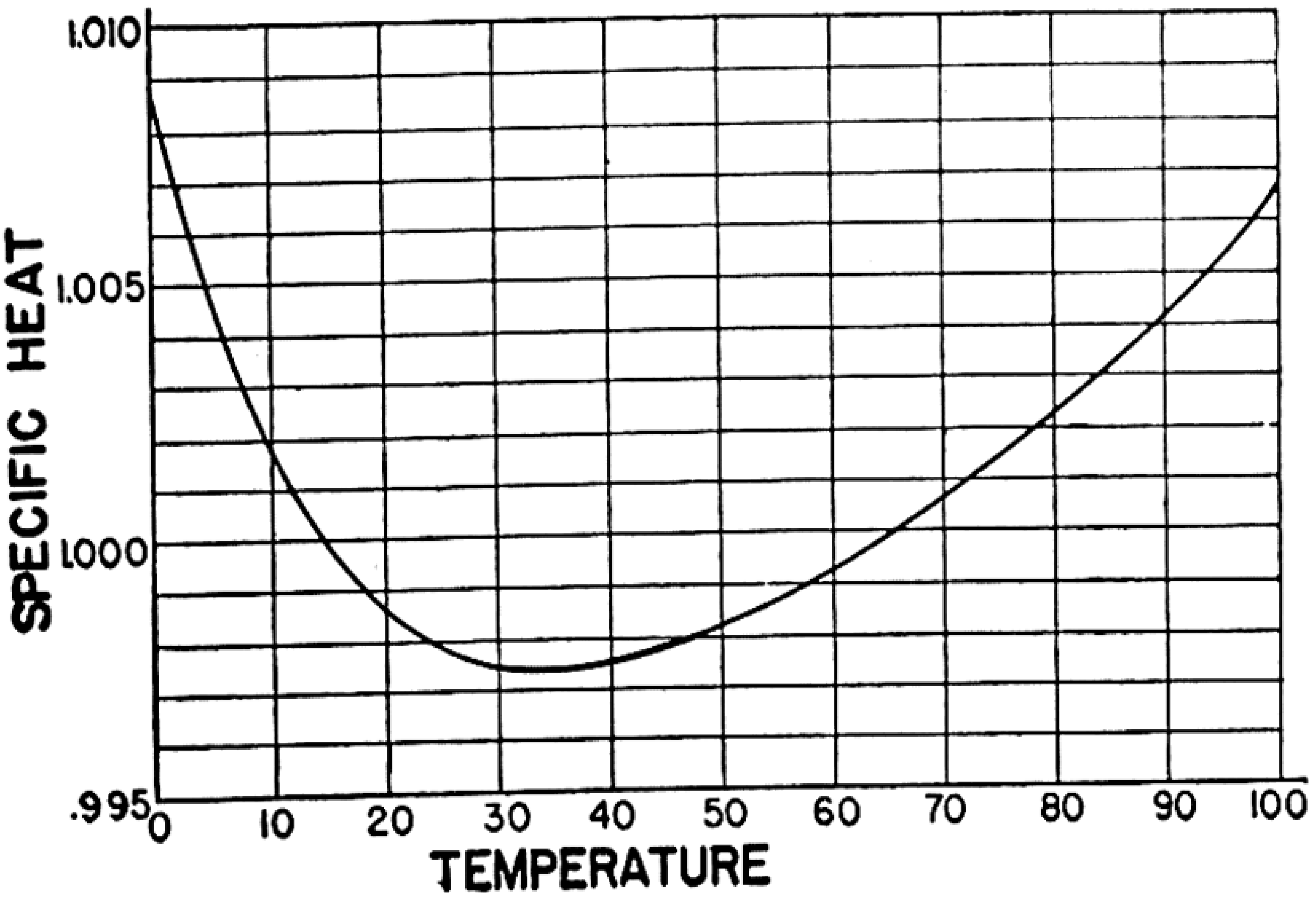

FIG. 23. The specific heat of water at temperatures between 0° C. and 100° C

that would raise the temperature of 1 gm. of water from 14.5° C. to 15.5° C. or from 65° C. to 66° C. This quantity is therefore spoken of as the " 15° " *calorie* and is the generally accepted unit for the measurement of heat. The " 20° " calorie, i.e., the quantity of heat required to change the temperature of a gram of water from 19.5° C. to 20.5° C., was used in many early investigations. Actually the average 100° calorie is slightly larger than the 15° calorie as can be seen from Fig. 23.

By definition the thermal capacity of a substance is the number of calories needed to raise the temperature of 1 gm. of that substance 1° C. Figure 23 thus shows graphically the variation in the thermal capacity of water with temperature. The thermal capacity of a body means the quantity of heat needed to change the temperature of the body 1° C. and is thus equal to the total mass times the thermal capacity of the substance. The term " specific heat of a substance " originally was defined as the ratio of the thermal capacity of a substance to the thermal capacity of water under identical conditions. Since the variation in the thermal capacity of water is not large (about

± ½ of 1% between 0° C. and 100° C.) it is usually assumed to be unity, and hence the specific heat of a substance and its thermal capacity are numerically identical. It is now common usage to define specific heat with exactly the same terms that are used to define thermal capacity. This quantity for a particular substance has a different value according as the body is maintained under different conditions during the addition of the heat; thus we have the specific heat under constant pressure, the specific heat under constant volume, the specific heat of a gas under constant saturation, etc.

In specific heat theory it is very often desirable to consider not 1 gm. of the substance but rather a number of grams equal to the atomic or molecular weight of the material. The corresponding specific heats are termed the atomic and molecular or molar specific heats.

Elementary Kinetic Theory. In an enclosed gas at a certain temperature a purely random distribution of the velocities of the particles as to direction exists. The magnitude of the velocities of the various particles varies greatly, in fact, no two particles should be expected to have exactly the same velocity. Some few particles might be expected to have very small velocities, and some will have very large velocities. In general, however, at a given temperature there will be a certain range in velocity for which the probability is a maximum. The distribution of velocity among the various particles may be represented graphically, as in Fig. 24. The equation of this curve is[10]

$$n = 4\pi N\, e^{-hmv^2} \cdot v^2 \cdot \left(\frac{hm}{\pi}\right)^{3/2} \tag{1}$$

In this equation, N represents the total number of particles, m the mass of each particle, and e the base of the Naperian system of logarithms. n is a quantity such that $n\,dv$ gives the number of particles with velocities between v and $v + dv$ and $h = 1/(2kT)$ where k is the gas constant per molecule, see page 49, and T is the absolute temperature. Hence areas in this figure represent numbers of particles, and equivalent areas under the two curves, as shown, denote the same total number of particles. This formulation, due to Maxwell, is called a Maxwellian distribution and appears to be applicable to many other physical properties when the meaning of the symbols is suitably modified. At a certain temperature there is a maximum in the curve at a certain definite velocity. As the temperature increases this peak moves toward larger velocities.

Another important quantity, namely, the " effective " velocity or the square root of the mean square velocity, may now be defined. To obtain this quantity, the velocity of each particle v is squared and summed for the total N molecules. This sum divided by the total number of particles gives the square of the effective velocity of the particles. This quantity is important in expressing the average kinetic energy of the particles. Thus

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[10] J. Jeans, *Dynamical Theory of Gases*, Fourth Edition, p. 33, 1925.

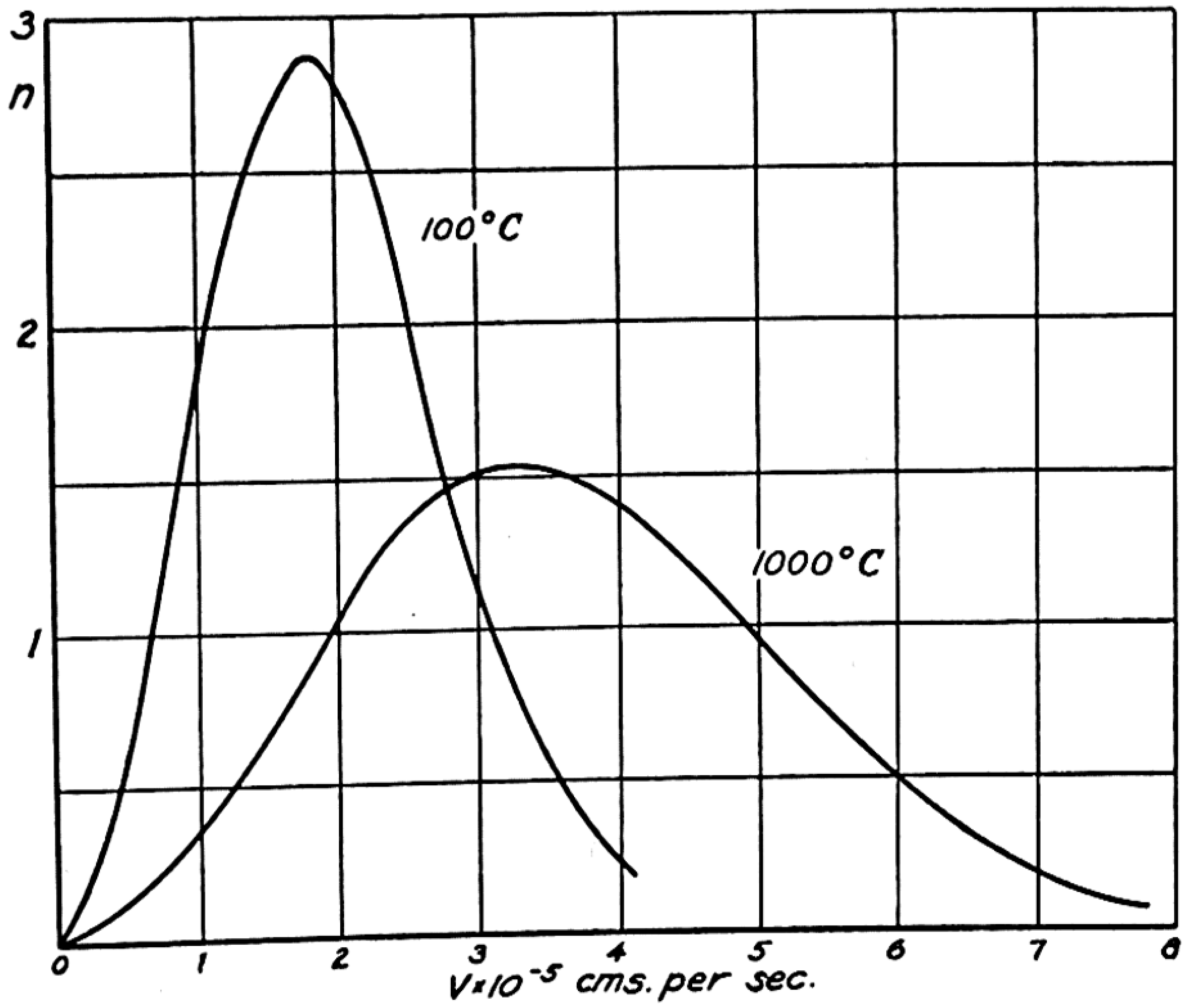

FIG. 24. The Maxwellian distribution of velocities for the particles of a gas.

$$v^2_{\text{eff.}} = \frac{1}{N}\sum_0^N v^2 \tag{2}$$

and the average kinetic energy per particle

$$\overline{\text{K.E.}} = \tfrac{1}{2}mv^2_{\text{eff.}} \tag{3}$$

where m is the mass of an individual particle.

Pressure. Let us imagine an elementary cube with an edge of unit length, having within it a single gas particle of mass m moving with a velocity v_x parallel to the edge in the X direction. The assumption of an edge of unit length somewhat simplifies the development and introduces no loss in generality in the final result. Upon elastic impact with the face of the cube, the particle rebounds with a velocity $-v_x$; hence from the law of conservation of momentum at impact, the YZ

face of the cube received a momentum of $2mv_x$. Now this particular face would receive such impacts $\frac{v_x}{2}$ times per second, since the particle must travel to the other face of the unit cube and back between impacts. Hence the pressure P which is the force F per unit area, which is in turn the momentum change Δmv per second per unit area, follows:

$$P = \frac{F}{A} = \frac{\Delta(mv)}{tA} = 2mv_x \cdot \frac{v_x}{2} = mv_x^2 \tag{4}$$

If there were N identical particles in the cubic centimeter acting independently they would contribute a pressure upon the YZ face of Nmv_x^2. However, for actual gases, experiment reveals the fact that the pressure on every face of the container is the same and moreover that the density at all points is sensibly uniform. This means that statistically as many particles per second pass through any plane in one direction as in the opposite sense, however the plane is oriented. For a random distribution of the velocities of the N particles the effective velocity $v_{\text{eff.}}$ may be formed and resolved into its components along the three axes X, Y, and Z of a mutually perpendicular system. It follows that

$$Nmv_x^2 = Nmv_y^2 = Nmv_z^2 = \tfrac{1}{3}Nm(v_x^2 + v_y^2 + v_z^2) = \tfrac{1}{3}Nmv_{\text{eff.}}^2 \tag{5}$$

The pressure P is then given by:

$$P = \tfrac{1}{3}Nmv_{\text{eff.}}^2 = \tfrac{1}{3}\rho v_{\text{eff.}}^2 = \tfrac{1}{3}\frac{M}{V} \cdot v_{\text{eff.}}^2 \tag{6}$$

where ρ denotes the density of the gas and M is the total mass of gas in a volume V.

The Gas Constant R. From the agreement for measuring temperature, by the normal thermometer together with the assumption of Boyle's law, the absolute temperature of a gas should be proportional to the product of its pressure P and its volume V. Then

$$PV = RT = \tfrac{1}{3}Mv_{\text{eff.}}^2 = \tfrac{1}{3}N'mv_{\text{eff.}}^2 \tag{7}$$

where N' denotes the total number of gas particles in the mass M and R is a proportionality factor called the gas constant. This quantity has a definite value only when complete information regarding the amount of gas is given. For different gases at the same pressure and temperature the values of R, if 1 gm. of each gas be considered, will be in the ratio of the specific volumes (i.e., volumes per gram) of the gases or inversely as their molecular weights. Thus

$$\text{(per gram)} \qquad \frac{R_1}{R_2} = \frac{\dfrac{P_1V_1}{T_1}}{\dfrac{P_2V_2}{T_2}} = \frac{V_1}{V_2} = \frac{(\text{M.W.})_2}{(\text{M.W.})_1} \tag{8}$$

A more significant value of R is one in which not 1 gm. but rather a gram-mole of each substance is considered. This must evidently be constant for all gases. This universal value of R is numerically

$$R = \frac{PV}{T} = 8313.6 \times 10^4 \text{ ergs deg. C.}^{-1} \text{ gm-mol.}^{-1} \tag{9}$$

or 1.986 cal. deg. C.$^{-1}$ gm-mol.$^{-1}$.

If the gas constant per gram-mole R be divided by the total number of particles per gram-mole N' there results a gas constant per particle ($k = R/N' = 1.3709 \times 10^{-16}$ erg per degree centigrade per particle). This number is frequently referred to as Boltzmann's constant.

If we combine, with equation 7, Avogadro's hypothesis that equal volumes of all gases under identical conditions of pressure and temperature contain equal numbers of particles, then it follows that at the same temperature the average kinetic energy per particle of all gases is the same. Thus whatever other forms of energy may be associated with the molecules of a gas, only their translational motion is important in determining the temperature. The velocities of the molecules of two gases in thermal equilibrium are thus inversely proportional to the square roots of the masses of the particles and hence inversely as the square roots of their molecular weights.

The Mean Free Path l of Gas Molecules. The average distance that a molecule travels between collisions with similar particles is an important quantity in kinetic theory. This distance may be readily expressed in terms of other quantities characteristic of the molecules, namely, their radii r (assumed spheres) and the number of particles per cubic centimeter N. A single spherical molecule of radius r, traveling with the mean velocity $\bar{v}$, sweeps out in one second a cylindrical volume $\pi r^2 \bar{v}$ cubic centimeters. The average volume occupied per particle is $1/N$ cubic centimeters. Molecules with their centers located within the radial distance $2r$ from the axis of the cylinder would project into it and hence suffer collision. Thus there would occur in one second $4\pi r^2 \bar{v} N$ collisions. The average distance l traveled between collisions (mean free path) is then $\bar{v}$ centimeters per second divided by the number of collisions per second, or

$$l = \frac{\bar{v}}{4\pi r^2 v N} = \frac{1}{4\pi r^2 N} = \frac{0.0795}{r^2 N} \text{ cm.} \tag{10}$$

The mean free path of the component particles of a gas should thus vary inversely with the pressure to which the gas is subjected, since N varies directly with the pressure.

This calculation has assumed that the other particles of the gas are

$P.V = \frac{1}{3}\rho v^2$

similar and at rest. If the velocities of the particles obey the Maxwellian distribution law then it may be shown[11] that the mean free path expected is somewhat less, so that

$$l = \frac{1}{4\sqrt{2}\pi r^2 N} = \frac{0.0562}{r^2 N} \text{ cm.} \tag{11}$$

This development is obtained by calculating the total distance traveled by all the molecules in any interval of time and dividing by twice the number of collisions occurring in the same interval. The factor 2 enters because each collision terminates two free paths.

This derivation is not unique. A development was carried out by Tait[12] in which the average was formed in a different manner. In his calculation the mean of the distances described by all the molecules was found when each molecule was allowed to trace out one free path, all beginning at the same instant of time. The result in this case was found to be

$$l = \frac{0.0538}{r^2 N} \text{ cm.} \tag{12}$$

These results are subject to further corrections if the effect of the walls of the container and the nature of the volume of the particle during collision be considered.

Jeans has shown that, if the " persistence of velocity " at collision be considered, assuming the molecules to be identical elastic spheres, then the mean free path must be multiplied by a factor 1.382 so that

$$l = \frac{1.382}{4\sqrt{2}\pi r^2 N} = \frac{0.0776}{r^2 N} \text{ cm.} \tag{13}$$

Since the radius of the particle is an unknown quantity, other relationships between these quantities l, r, and N must be found to allow their evaluation. Many such relationships from which r may be found are available. Of these may be mentioned those coming from (*a*) viscosity measurements, (*b*) x-ray measurements, (*c*) compressibility of the gas.

The values of r computed from the viscosity determinations (see page 52) agree approximately with the results deduced from the study of x-ray diffraction patterns. A determination of the constant b in van der Waals' equation of state representing the gas (see page 210) also gives information regarding the radius of the gas particles. The constant b is shown to be equal to $\frac{16}{3}N\pi r^3$, so that if N is known then r may be found. Values of r so determined agree approximately with those obtained by the other previously mentioned methods.

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[11] See, for example, J. Jeans, *The Dynamical Theory of Gases*, p. 37, 1925.

[12] P. G. Tait, *Proc. Roy. Soc.* (*Edinburgh*), **15**, 225 (1889).

For hydrogen at 0° C. and a pressure of one atmosphere the following approximate values are obtained: $\bar{v} = 169{,}500$ cm. per sec., $2r = 1.2 \times 10^{-8}$ cm. and $l = 1.42 \times 10^{-5}$ cm.

The Viscosity of a Gas and Its Variation with Temperature, Experimental. If a portion of the fluid in a given volume is set in motion with respect to other portions of the fluid and then left to itself, soon this relative motion will vanish completely. This is accomplished by a transfer of momentum from the more rapidly moving portion. Because of this ability to transfer momentum the fluid is said to be viscous and a coefficient of viscosity to express the property may be defined. If a surface of the fluid moves with a velocity Δv relative to a parallel plane at a distance Δy, then every square centimeter of the second surface will be acted upon by a tangential force F, tending to give it the velocity of the first surface, or vice versa. The coefficient of viscosity η is defined as follows:

$$\eta = \frac{F/A}{\Delta v/\Delta y} \tag{14}$$

When the force is 1 dyne per sq. cm. for a layer at a distance of 1 cm. moving with a velocity of 1 cm. per sec., the coefficient of viscosity is said to be 1 poise. The fundamental dimensions are thus dynes per square centimeter per second. For gases the values are usually expressed in terms of millionths of this unit. Thus for air at 20° C. η is 180 μp (micropoise) and for hydrogen at the same temperature the value is 88 μp. The viscosity of liquids is usually expressed in hundredths of the poise. Thus for water at 20° C. the value is 1.005 centipoise.

Since the force is fundamentally the momentum communicated per second it may be calculated from kinetic theory. Maxwell expressed the viscosity of a gas in terms of the mass of the particle m, the average velocity $\bar{v}$, the number of particles per cubic centimeter N, and the mean free path l as follows:

$$\eta = \tfrac{1}{3}Nm\bar{v}l = \tfrac{1}{3}\rho\bar{v}l \tag{15}$$

where ρ is the density.

On introducing the value of the mean free path l from equation 13 together with a numerical correction factor due to Chapman,[13] the coefficient of viscosity η becomes

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[13] S. Chapman, *Roy. Soc. Phil. Trans.*, **216**, 279 (1916).

$$\eta = 0.028\,\frac{m\bar{v}}{r^2} \tag{16}$$

From equation 6 the pressure P was $\frac{1}{3}\rho\bar{v}^2$ which may be combined with equation 15 to relate the mean free path and the viscosity as follows

$$l = \eta\sqrt{\frac{3}{P\rho}} \tag{17}$$

The viscosity of the fluid is evidently of utmost importance in problems of flow. A simple formula was developed by Poiseuille to express the volume V of fluid transferred per second by a tube of length L, of small radius R having a difference of pressure between the two ends of the tube of ΔP, namely,

$$V = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot l \cdot \eta} \tag{18}$$

Many other more realistic formulations of this relationship have been made.[14]

An experimental arrangement for determining the viscosity of a gas and its variation with temperature is shown in Fig. 25. This makes use of the equation of Poiseuille or any equivalent relationship for the rate of flow. By the electrolysis of water a definite amount of hydrogen and oxygen are set free each second. These gases are conveyed through the calibrated capillary tubes maintained at any desired temperatures. By varying the electric current the rate of production may be adjusted to give a desired steady pressure if the diameter of the capillary is properly chosen. The pressure difference is given directly by each manometer. On determining the viscosity η at several temperatures, it is instructive to plot the values of log η against log T. The slope of this line gives the effective power of T in influencing viscosity.

From equation 16 it might be expected that since the viscosity of a gas appears to depend on $\bar{v}$, it would vary as the square root of the temperature of the gas. In practice this is found to be not precisely true. As would be expected, the viscosity is independent of the pressure except at very low and at high pressures. In liquids the viscosity decreases as the temperature increases.

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[14] E. Buckingham and J. D. Edwards, *Sci. Papers, U. S. Bur. Stand.*, **15**, 573 (1920).

The Difference between the Molar Specific Heats of a Gas C_p and C_v. If the temperature of a gram-mole of a gas be elevated 1° C. under the condition of a constant pressure P, a quantity of heat C_p will be required. The quantity C_p is evidently greater than that quantity needed to raise the temperature of the same mass 1° under the condition of constant volume C_v. This follows from the fact that in the

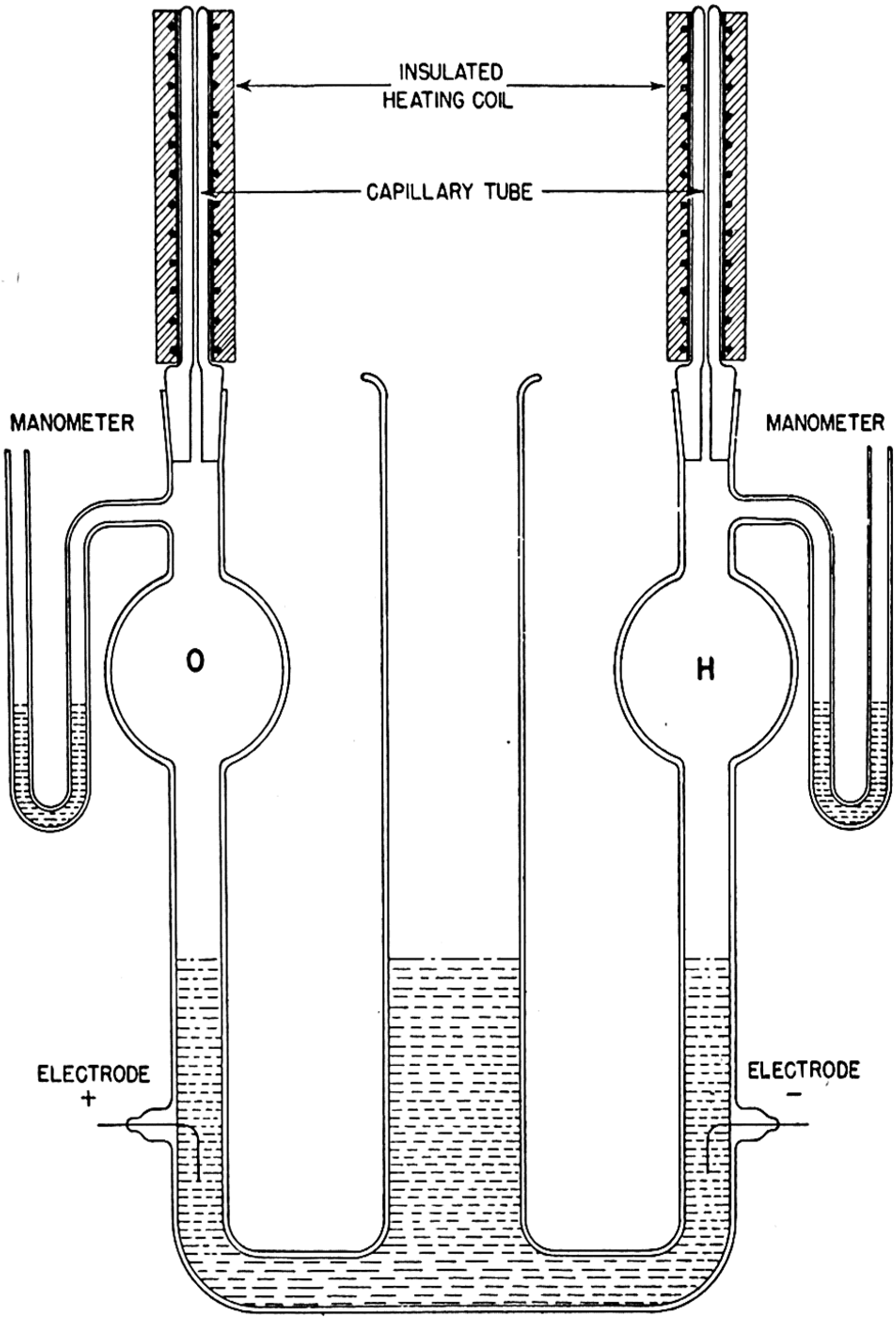

FIG. 25. Apparatus to measure the viscosity of a gas and to observe its change with temperature.

former case the volume V increased by an amount ΔV, and consequently external work to the amount $P \cdot \Delta V$ is done. This work is in addition to the increase in the internal energy of the gas which alone occurs in the latter case.

Hence it follows, by introducing the factor J (mechanical equivalent of heat) to change work units to heat units, that

$$C_p = C_v + \frac{P \cdot \Delta V}{J} \tag{19}$$

But from the gas law ($PV = RT$) for constant P, $P \cdot \Delta V = R \cdot \Delta T$. The change in temperature ΔT involved in C_p or C_v is $\Delta T = 1°$. Thus

$$C_p = C_v + \frac{P \cdot \Delta V}{J} = C_v + \frac{R \cdot \Delta T}{J} = C_v + \frac{R}{J} \tag{20}$$

and hence

$$C_p - C_v = 1.986 \frac{\text{calories}}{\text{gm-mol. deg. C.}} \text{ for all gases} \tag{21}$$

Ratio of Specific Heats C_p/C_v for Gases. An important quantity in the field of heat, for gases, is the ratio of the specific heat under constant pressure to that under constant volume ($C_p/C_v = \gamma$).

The importance of this quantity lies in the fact that it enters in many related phenomena involving the substance, as, for example, in the expression for the velocity of sound in the gas. The magnitude of γ for a gas, on the basis of classical theory, at once reveals considerable information about the complexity of the molecules of which the substance is composed. This relationship may be shown by rewriting equation 7 for a gram-mole of the gas so as to introduce the average kinetic energy (K.E.) of the gas particles. Thus

$$RT = \tfrac{1}{3}N'mv^2 = \tfrac{2}{3} \cdot N' \cdot \tfrac{1}{2}mv^2 = \tfrac{2}{3} \cdot (\text{K.E.}) \tag{22}$$

But for a monatomic gas (K.E.) denotes the total internal energy, since for this, only translational motion in three dimensions is possible. It is thus customary to associate with the kinetic energy three degrees of freedom ($f = 3$). The energy per degree of freedom is therefore

$$\tfrac{1}{3}(\text{K.E.}) = \tfrac{1}{2}RT \tag{23}$$

Then, in general, for f degrees of freedom the total energy U is, by the "equipartition" principle:

$$U = f(\tfrac{1}{2}RT) \tag{24}$$

The molecular specific heat under constant volume (C_v) (i.e., the rate of change of energy U with temperature T) must then become

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = f \cdot \frac{R}{2} \tag{25}$$

The molecular specific heat under constant pressure follows from equation 20 as

$$C_p = C_v + R = \left(\frac{f}{2} + 1\right)R \tag{26}$$

Then dividing equation 26 by equation 25 the final expression for γ is obtained:

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f} \tag{27}$$

For a mass point gas, such as the metallic vapors or the noble gases helium, argon, krypton, and neon, only translational motion would be possible and $f = 3$, giving $\gamma = 1.66$, a result agreeing well with experiment. The value of γ observed for diatomic gases is in general 1.4, indicating a value of f equal to 5. This is readily explained if the diatomic molecule be assumed to possess the form of a dumbbell. The two additional degrees of freedom are considered as due to the possibility of rotation about two axes mutually at right angles to each other and to a line through the centers of the atoms. For an axis through the centers, the moment of inertia is insignificant and hence this rotation contributes little to the specific heat. Vibration of the atoms within the molecule is believed to contribute an effect only at higher temperatures.

For many triatomic molecules the value of γ is 1.33 or less, indicating the existence of additional degrees of freedom, as would be expected from any model of the molecule. If one follows closely the equipartition principle, partial degrees of freedom must be allowed as well as a gradual variation in f with temperature. At higher temperatures the value of γ becomes smaller. This could be explained by assuming the introduction of vibrational motion in the molecules. This would increase both C_p and C_v and hence would result in increasing both the numerator and denominator of the improper fraction of equation 27 by the same amount and would thus decrease the quotient.

Adiabatic Transformation; Gases. When the condition of a given amount of gas is altered in any way and no quantity of heat is added to, or taken from, the substance, then an adiabatic change is said to have taken place. It is the purpose of the following development to show that, if the initial conditions and certain facts regarding the final state are known completely, then complete information regarding the final state may be determined.

If a gram-mole of the substance be considered as undergoing an elementary change in temperature dT, and a change in volume dV, and any heat added or subtracted be denoted by dQ, then for the adiabatic process

$$dQ = C_v\,dT + P\,dV = 0 \tag{28}$$

By differentiation of the expression for the gas law and substituting for R its value in equation 21, it follows that:

$$P\,dV + V\,dP = R\,dT = (C_p - C_v)\,dT =$$

$$(C_p - C_v)\,\frac{-P\,dV}{C_v} = (\gamma - 1)\,(-P\,dV) \tag{29}$$

Separating the variables, using the first and last members of equation 29, gives

$$\gamma\,\frac{dV}{V} = -\,\frac{dP}{P} \tag{30}$$

which by integration leads to

$$PV^{\gamma} = C \text{ (Constant)} \tag{31}$$

From the gas law $P = (RT)/V$, so that

$$TV^{\gamma-1} = \frac{C}{R} = C_1 \tag{32}$$

and

$$T^{\gamma}P^{1-\gamma} = \frac{C}{R^{\gamma}} = C_2 \tag{33}$$

C, C_1, and C_2 are related constants.

Thus if the initial pressure, temperature, and volume be known, and any one of the values, pressure, temperature, or volume in the final state, then the remaining two final quantities may be determined.

Specific Heats — Experimental. The specific heats of various substances are generally obtained experimentally under the condition of constant pressure. The procedure usually employed may be classified under the following methods:

a. Method of mixtures.
b. Ice calorimeter.
c. Method of cooling.
d. Condensation method.
e. Electrical method.

Under each of these headings many forms of apparatus may be employed. The descriptions herewith given are intended only as representative of the apparatus of each type.

Method of Mixtures. One of the earliest methods of measuring the specific heat of substances C_p was the method of mixtures. As the name implies, a body of the material under investigation at a certain temperature T_1 is allowed to come in close thermal contact with another body of material of known specific heat C_p at a temperature T_2, where $T_2 \neq T_1$. The resulting mixture attains an intermediate equilibrium temperature T. Thus a hot body, such as a piece of metal of mass M_1 at T_1, may be dropped into a calorimeter containing a mass M_2 of water at a temperature T_2. Then

$$M_1(C_p)_1(T_1 - T) = M_2(C_p)_2(T - T_2) \pm \text{Heat losses} \tag{34}$$

If the heat losses are known or accounted for, then one unknown quantity such as the specific heat of the metal (C_p) may be obtained from the equation. The equilibrium temperature T is not always determined straightforwardly, on account of radiation effects. It was suggested first by Count Rumford that errors due to losses in heat by radiation may be practically eliminated if by a preliminary trial $(T - T_2)$ be determined and then the temperatures adjusted so that in the final experiment T_2 was as much below the temperature of the room as the equilibrium temperature T was above it. This is not quite exact, as may be seen from Fig. 26, which represents the changing temperature in the receiving calorimeter, with time. T_0 represents the temperature of the room. If Newton's law of cooling is assumed to hold for the heat transferred to and from the surface of the calorimeter, then one sees that T_0 should be arranged with T and T_2 so that the areas T_2ab and Tbc are equal, that is, $(T_0 - T_2)$ must be greater than $(T - T_0)$.

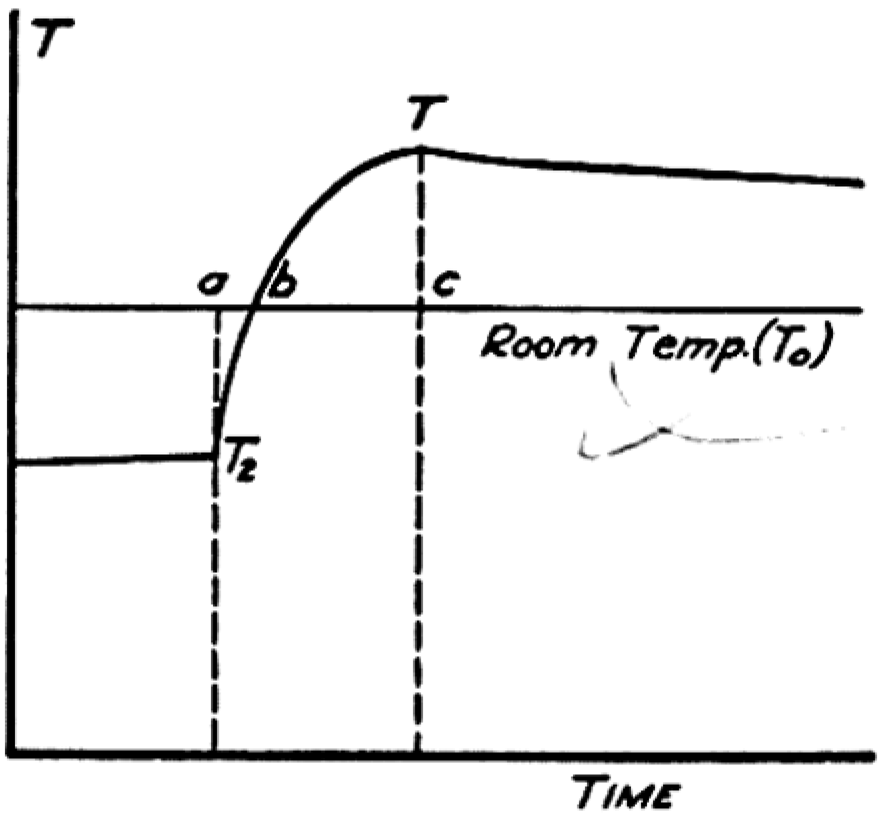

FIG. 26. Adjustment of initial and final temperatures to minimize radiation errors.

In any experiment, even where T_2 is greater than T_0, the correction ΔT, to be added to the maximum observed temperature T_a to give the correct temperature T, is readily found. Newton's law of cooling states that the rate of loss of heat from a body is proportional to the difference in temperature between the body and its surroundings. Considering the thermal capacity of the body constant then the time rate of cooling is also proportional to the temperature difference so that

$$\frac{dT}{dt} = c(T - T_0) \tag{35}$$

where c is a constant involving the thermal capacity of the body. By integration this yields

$$\log (T - T_0) = C_1 t + C_2 \tag{36}$$

in which C_1 and C_2 are constants. Thus $\log (T - T_0)$ is linear when plotted with the time t as shown in Fig. 27. To obtain the corrected temperature T_c, this curve should be extrapolated not to zero time but to an intermediate time which is determined graphically.

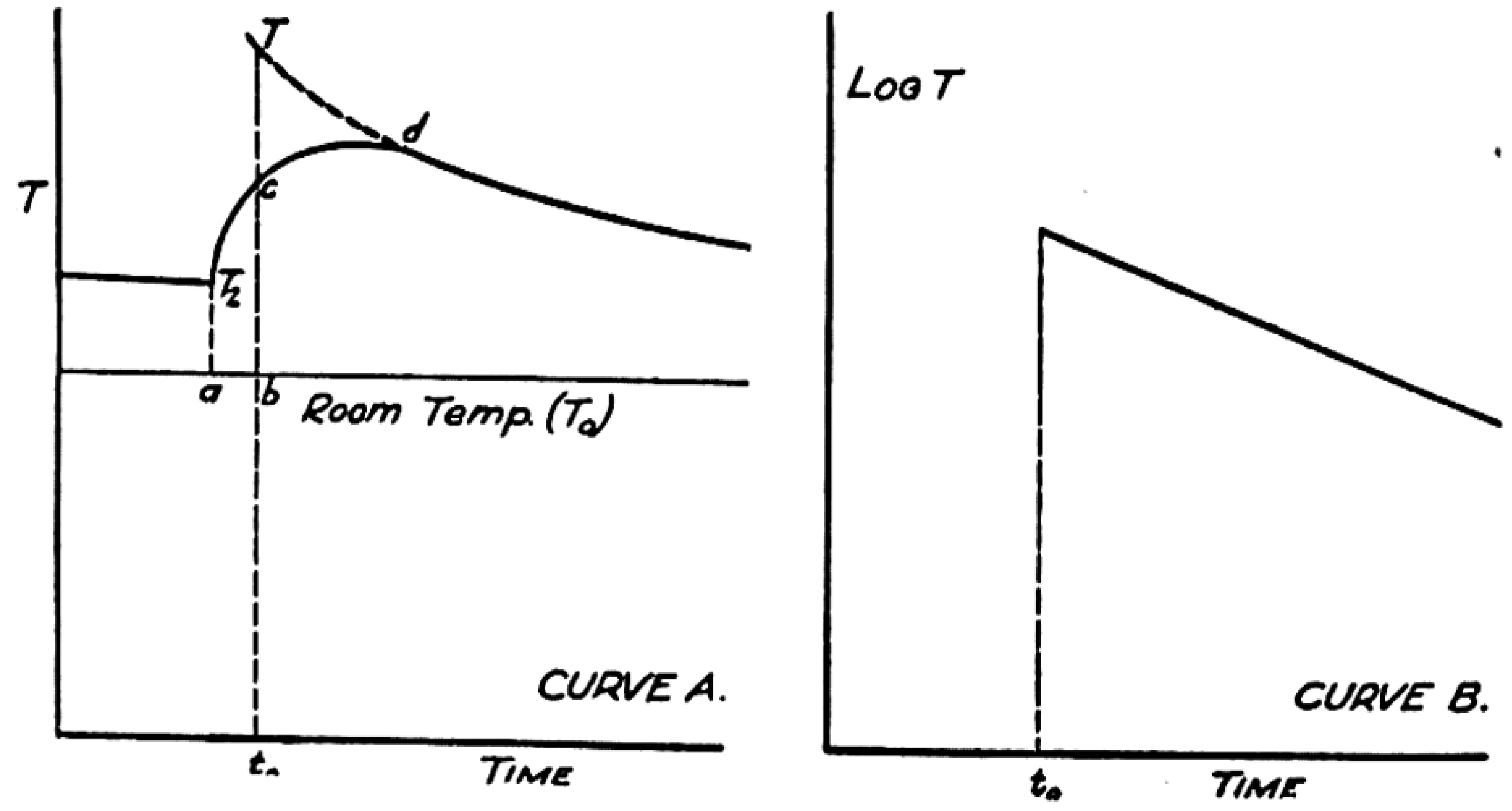

FIG. 27. Temperature-time and logarithm of temperature versus time for a radiating body.

A method of correcting for the effect of radiation in heating a calorimeter is shown in Fig. 28a. By observing the temperature fall per minute at the end, called dT, where the temperature difference between calorimeter and surroundings is m, it is possible to compute the corrections for each minute during the heating process. Thus for the first minute d_1T is $(a/m) \times dT$; d_2T is d_1T plus $(b/m) \times dT$; d_3T is d_2T plus $(c/m) \times dT$; etc. The corrected maximum temperature is T_2 and the effective temperature change is $(T_2 - T_1)$.

In dropping the specimen from the source of high temperature T_1, precautions against losses in heat by radiation should be observed. An illustration of the technique that may be employed may be found by referring to the very extensive experiments of W. P. White[15] on this subject. In these investigations the specific heats of substances have been determined at very high temperatures and hence losses of heat by radiation would have been very significant. In the manipulation, the specimen under investigation was contained in a refractory shell, which had previously been dropped empty. By combining the results obtained when the empty shell was dropped with the result obtained when the shell and specimen together were used, a difference effect due solely to the contents of the shell could be calculated.

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[15] W. P. White, *Am. Jour. Sci.*, **47**, 44, 1919, *et seq.*

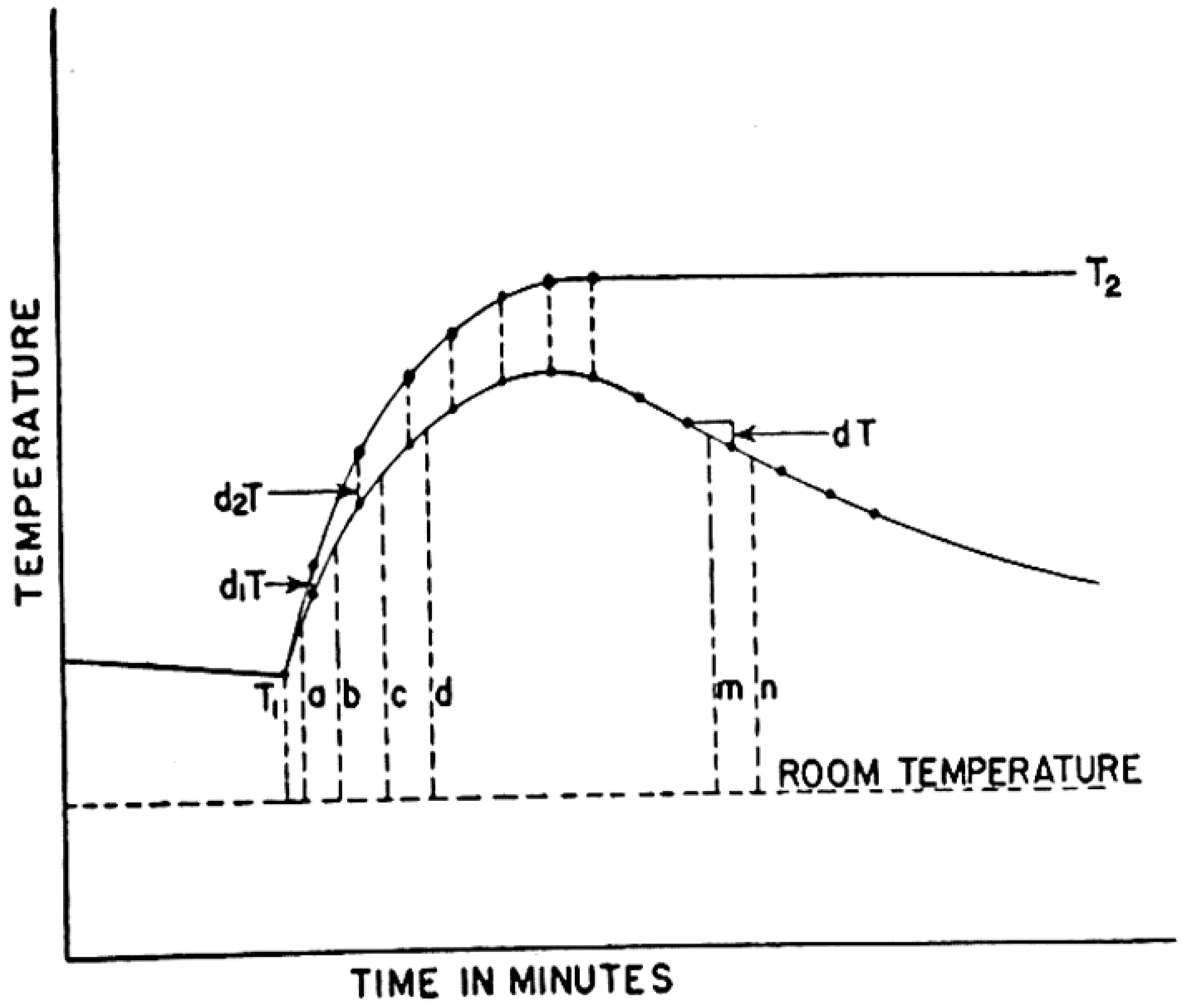

FIG. 28*a*. Corrections to observed temperatures to give the highest temperature attained.

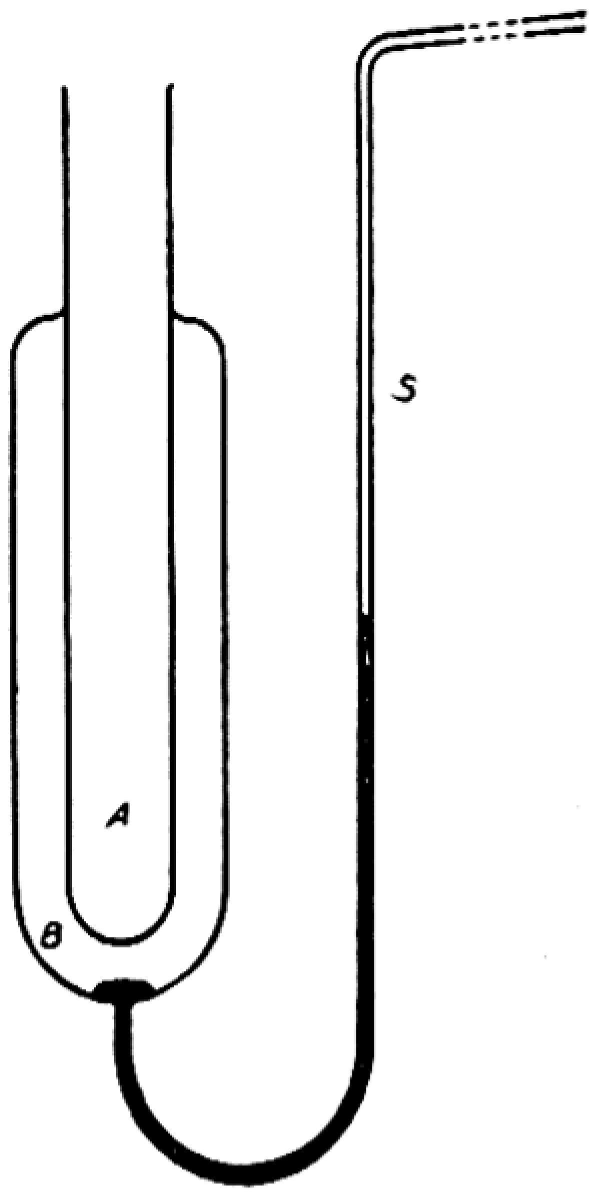

FIG. 28*b*. The Bunsen ice calorimeter.

Another arrangement[16] that has been used to reduce heat losses by radiation is to surround the calorimeter with a jacket whose temperature is kept at all times very nearly equal to that of the calorimeter. This may be accomplished by some independent means such as an electrical heating circuit. Devices of this sort are called "adiabatic" calorimeters.

Modern vacuum bottles when used as calorimeters are able to reduce to an insignificant quantity the otherwise fairly large heat loss due to radiation.

A special form of the method of mixtures is the method of stationary temperatures proposed by Hesehus.[17] It consists in adding enough cold water to the calorimeter immediately after dropping the specimen from a high temperature to maintain the calorimeter always at room temperature.

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[16] T. W. Richards, *Jour. Am. Chem. Soc.*, **31**, 1275 (1909); G. Lange, *Zeit. Phys. Chem.*, **110**, 343 (1924).

[17] N. Hesehus, *Jour. Phys.* **7**, 489 (1888).

Ice Calorimeter. One of the earliest forms of quantitative calorimetric apparatus has been attributed to Joseph Black who made use of the fact that a definite mass of solid, in changing into a liquid, with no change in temperature, absorbs a definite quantity of heat. In the method of Black the specimen whose specific heat was to be found was dropped from some source at a high temperature T_1 into a cavity in dry ice. A cover consisting of a block of dry ice was placed over the cavity. The specimen in cooling to the melting point of ice liquefied a definite mass of ice M_w, which was then separated and weighed. Denoting the latent heat of fusion of ice by L, the mass of the specimen by M_x, and the specific heat of the specimen by C_p, then:

$$M_xC_p(T_1 - 0) = M_wL \pm \text{Losses of heat} \tag{37}$$

Heat losses due to radiation, except that which occurs in the dropping process, are negligible, since they produce only a melting on the outside of the block of ice. The most difficult part of the manipulation is correctly to separate and weigh the water melted, because of its tendency to adhere to the ice walls of the chamber.

The ice calorimeter reached its most sensitive form in the apparatus of Bunsen.[18] This device is represented in Fig. 28*b*. The bulb B is first filled with pure water free from air, and then a small quantity of the water is displaced with mercury. The whole apparatus is now placed in an outer container of ice and allowed to come to a temperature 0° C. By lowering a freezing mixture into the inner bulb A (carbon dioxide snow or liquid air is very satisfactory), a portion of the water in B is frozen, causing a consequent increase in volume. This increased volume forces the mercury up the capillary tube S. When the upper surface of the mercury attains a position at the top of the scale the freezing agent is removed and the temperature is allowed to become constant at 0° C. The specimen under investigation, at some temperature T_1, is lowered into the bulb A. When a steady state is obtained the lowering of the mercury in the tube S is observed. A definite amount of water at a known temperature may now be added to A to calibrate the scale. The value[19] of the density of ice (0.916 gm. per cm.^{3}) together with a knowledge of the diameter of the capillary tube allows one to calculate the sensitivity of the apparatus in calories per scale division. Under favorable conditions a very high sensitivity is obtained. This allowed Bunsen to determine the specific heats of many rare metals, obtainable only in small quantities. If the chamber B were placed directly in an ice bath, there is generally a creep-ing of the level of the mercury in the scale, owing to a slight difference in the freezing point of the two specimens of water. This drift may be almost completely eliminated by surrounding the outer tube with a layer of material which is a poor conductor of heat.

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[18] R. Bunsen, *Phil Mag.*, **41**, 161 (1871).

[19] E. L. Nichols, *Phys. Rev.*, **8**, 21 (1899).

Condensation Method. One of the most sensitive calorimetric devices available is the differential steam calorimeter as developed by Joly.[20] So delicate is the indication of the instrument that its most important application has been in the determination of the specific heat of gases under constant volume — a quantity until that time considered incapable of measurement. The apparatus as used by Joly is shown in Fig. 29. In this instrument a sensitive beam balance supports two hollow metal spheres as nearly alike as possible. To test the identity of the spheres a preliminary test is made with both spheres evacuated. Then, with one sphere empty and the other filled with the gas under investigation all at an equilibrium temperature T_1, dry steam is allowed to enter the chamber. This steam, upon coming in

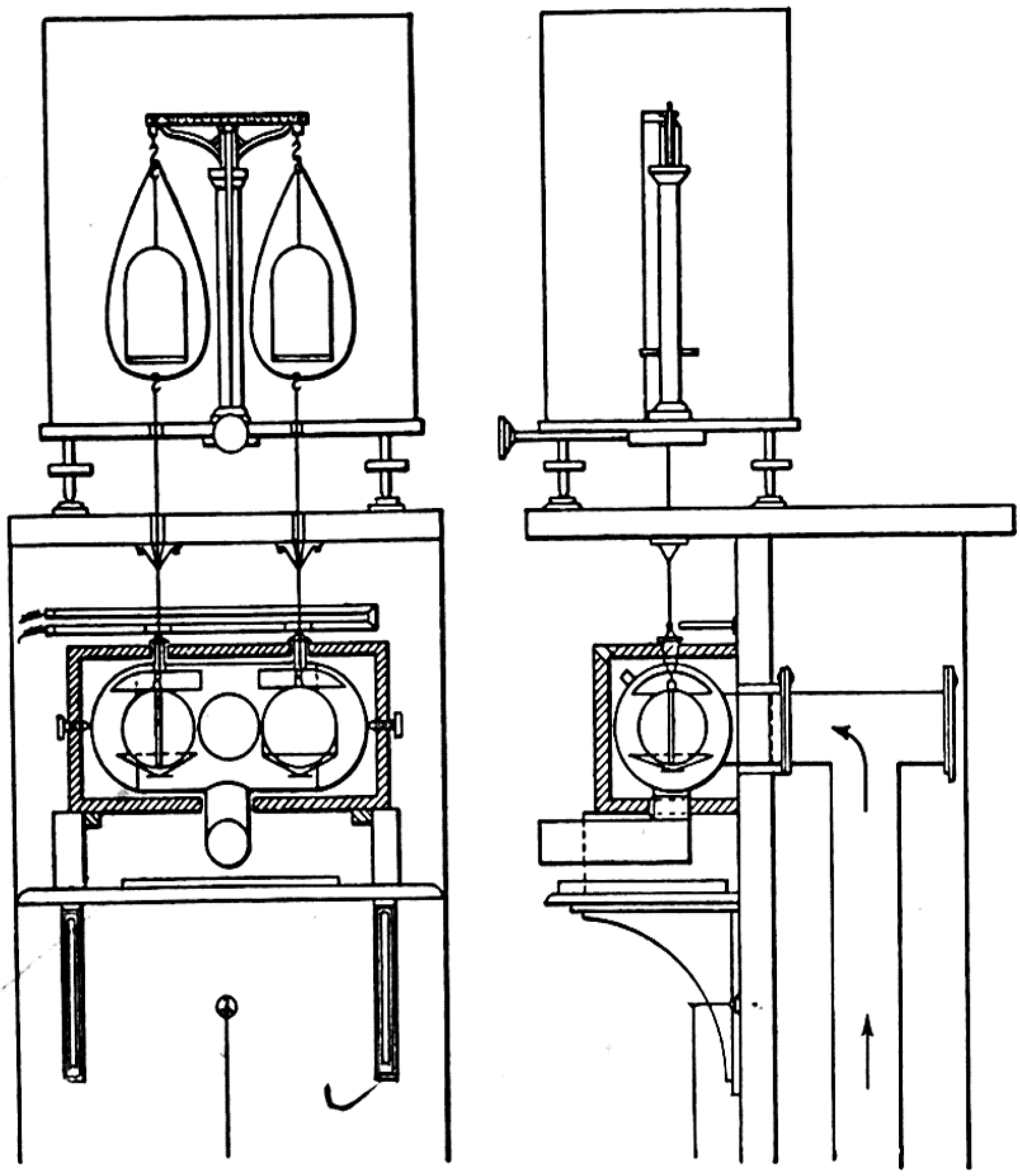

FIG. 29. The Joly steam calorimeter.

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[20] J. Joly, *Proc. Roy. Soc.* (*London*), **41**, 352 (1886).

contact with the colder bodies, gives up its heat content and in part condenses and is collected in the underhanging pans. Soon the temperature of the whole chamber will attain that of the condensation point of the steam and no further condensation will occur. The pan beneath the sphere containing the gas will now have in addition the amount of water condensed by the contained specimen of gas. Since the expansion of the metallic spheres is relatively small, the specific heat involved is that under constant volume C_v. Thus

$$(W_2 - W_1)L = M_x(C_v)(100 - T_1) \pm \text{Losses} \tag{38}$$

where L denotes the latent heat of vaporization of water, M_x the mass of gas of specific heat C_v, at the initial temperature T_1, and $W_2 - W_1$ is the weight needed to restore a balance. The effect of the empty sphere is thus to render the thermal capacity of the container of the gas zero. For precise results, correction must be made for the expansion of the spheres both thermal and elastic. The results of Joly showed that for air the specific heat increased, whereas for hydrogen the specific heat decreased, with increased pressure.

Electrical Method. The electrical method in various forms is perhaps one of the most commonly employed methods in calorimetry. This depends upon the now well-established relationship between the calorie and the unit of electrical energy. The method has been employed with great care, by E. Griffiths and E. H. Griffiths,[21] in the determination of the specific heats of various metals.

If E represents the potential difference between the terminals of the heater coil, I the current through it, and J the mechanical equivalent of heat, then the power supplied in calories per second is

$$\frac{EI}{J} = m_x(C_p)\frac{dT}{dt} \pm \frac{\text{Energy loss}}{\text{Second}} \tag{39}$$

where m_x is the mass of the specimen heated, C_p is its specific heat, and dT/dt is the rise in temperature per second. Since the electric power can be measured with considerable accuracy, the success of the method depends on how accurately account is taken of the losses by radiation. In vacuum flasks or with containers having independently heated jackets at the same temperature as the calorimeter, these losses may be reduced to a minimum.

In a modification of this method, known as the continuous-flow method, the specimen (a fluid) is made to pass with a uniform velocity through a chamber heated by supplying power at a constant rate. In the steady state when losses by radiation have been accounted for, a constant difference in temperature ($T_2 - T_1$) will exist between the fluid entering and that leaving the chamber. If ρ_x represent the density of the fluid, C_p its specific heat, and dV/dt the volume of fluid passing per second, then

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[21] E. H. and E. Griffiths, *Phil. Trans.*, **214** A, 319 (1914).

$$\rho_x(C_p) \cdot \frac{dV}{dt} \cdot (T_2 - T_1) = \frac{EI}{J} \pm \text{Losses} \tag{40}$$

This method has been employed for air and for helium and other rare gases at low temperatures (−180° C. to 20° C.) by Scheel and Heuse.[22] With the method suitably modified by Holborn and Jakob,[23] the specific heat of air at pressures as high as 1,200 atmospheres has been determined. The effect of losses by radiation may sometimes be eliminated by using widely different rates of flow but adjusting the heater current so that the rise in temperature for each rate of flow is the same. Since the losses by radiation are then the same in both cases, they disappear upon forming the difference of the two equations. However, in forming the difference or the sum of two measured quantities each with an uncertainty, the result has an uncertainty equal to the sum of that of the individual measurements. Hence the final result is not so free from error as might be hoped.

Radiation Methods. When a substance is allowed to cool from a high temperature in surroundings at a lower temperature, the rate of cooling depends upon various factors. The character of the surface as well as its total area and its thermal relationship with the surroundings determine the rate of giving up heat. The water equivalent of the radiating body will determine how rapidly this heat loss will diminish the temperature. Let the function which represents the influence of the temperature T of the body upon its rate of radiation be represented by $F(T)$. If A stands for the area of the radiating surface and R the energy radiated per square centimeter per second, when the temperature of the body is 1° above that of its surroundings, then the total energy radiated in the time Δt is $RA(\Delta t)F(T)$. This will lower the temperature of the body, whose thermal capacity is $m_x(C_p)$, by an amount ΔT, so that

$$RAF(T) \cdot \Delta t = m_x(C_p) \cdot \Delta T \tag{41}$$

If we wish to compare the specific heats of several liquids, equal volumes of the liquids may be placed in silvered test tubes which are as nearly as possible identical. These are suspended in surroundings at a common temperature T. The intervals of time Δt required for the various tubes to cool through some particular definite range of temperature ΔT, such as from 50° C. to 49° C., are observed. Under these conditions the quantities R, A, and $F(T)$ are the same in every case. Hence

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[22] K. Scheel and W. Heuse, *Ann. Physik.*, **37**, 79 (1912).

[23] L. Holborn and M. Jakob, *Zeit. Ver. deutsch. Ing.*, **58**, 1429 (1914).

$$\frac{\Delta t_1}{\Delta t_2} = \frac{m_1(C_p)_1 + k}{m_2(C_p)_2 + k} \tag{42}$$

where k denotes the constant water equivalent of the unfilled tube or bulb.

This method may readily be combined with an electrical method to determine the absolute rather than the relative value of the specific heat. Thus, if an electric heater coil is placed in the material under investigation, one can apply a certain amount of power and await an equilibrium of temperature. In the steady state, heat is being radiated from the surface of the body just as fast as it is being received from the electrical source. The rate of supply is readily measured and hence yields the rate of radiation at the particular temperature of equilibrium. By changing the power rate a new temperature of equilibrium is obtained and successively, one can obtain the radiation at various distributed temperatures. These values may be plotted, thereby giving a power (radiation)-temperature curve as shown in curve A, Fig. 30.

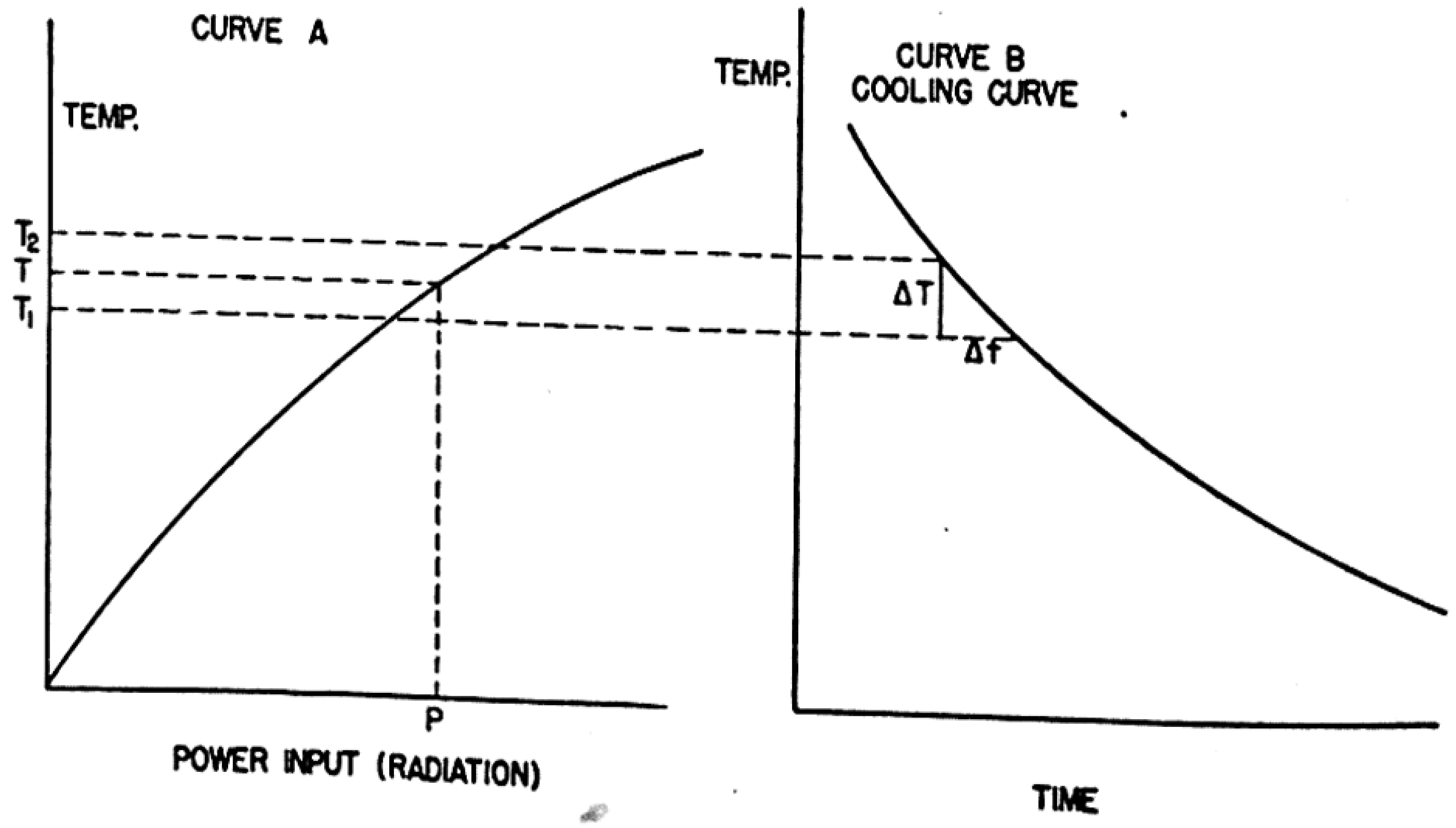

Fig. 30. Curves for the determination of specific heat by the method of radiation.

The specimen is now allowed to cool from the higher temperature attained, keeping the surroundings identical. This cooling curve is shown in curve B, Fig. 30. By using a common scale of temperature as ordinate, two parallel horizontal lines may be drawn, as shown in Fig. 30, intersecting the two curves. From the intersections in curve A may be observed an average radiation rate $\overline{P}_T$, at the chosen temperature T. From the intersections in curve B is observed the time Δt corresponding to a cooling of the specimen through the same temperature range ΔT. Then

$$\Delta t \cdot \overline{P}_T = M_x(C_p)_x \cdot \Delta T \tag{43}$$

from which C_p can be evaluated. This can be set up for several temperature intervals so that the variation in specific heat with temperature can be observed.

THE RATIO OF THE SPECIFIC HEATS (γ) FOR GASES

Experimental Method of Clément and Désormes. The ratio of the specific heat of a gas under constant pressure to that under the condition of constant volume, γ, may be measured experimentally in several ways. One interesting method was originally due to Clément and Désormes.[24] This apparatus as modified for laboratory use is shown in Fig. 31. A large gas-tight bulb is fitted with a poppet valve V at the top and a sensitive manometer M open to the air. The flask is coated with an insulating layer to increase the time required to establish thermal equilibrium. The gas to be studied is introduced into the bulb under a pressure P_1 slightly in excess of the atmospheric pressure P_0, so that in the manometer M, b stands slightly above a. After the gas has attained a steady temperature (manometer constant) the poppet valve V is given a tap. This momentarily connects the inner space with the atmosphere and P_1 falls to P_0. The adjustment of pressure takes place so rapidly that the transfer of heat is not allowed, and so the expansion may be regarded as purely adiabatic. In forcing some gas out of the bulb to establish atmospheric pressure, the remain-

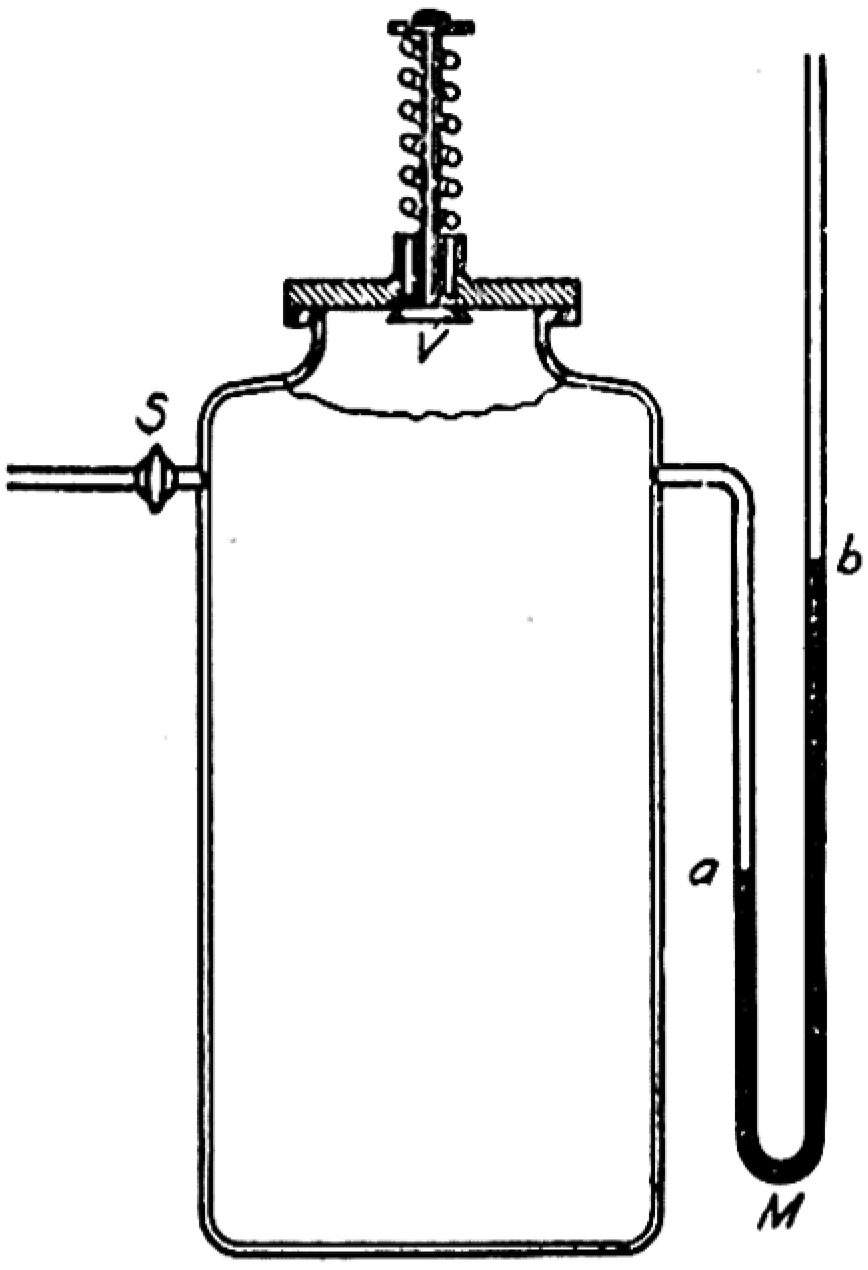

FIG. 31. Apparatus of Clément and Désormes for the ratio of the specific heats of a gas.

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[24] M. Clément and C. B. Désormes, *Jour. phys.*, **89**, 320 (1819).

ing gas will be cooled. Now if the bulb and contents are allowed to stand, the gas will again soon assume the temperature of the room, with an accompanying increase in pressure to a new value P_2 greater than P_0 but less than P_1. In the final state the gas is again at the temperature of the room, and hence the initial and final states are connected by the isothermal gas relationship while the initial and intermediate states are connected by the relationship for adiabatic processes. Hence, considering not the whole amount of gas but, say, unit mass at the center of the bulb, since some gas escaped, and letting V_1, V_0, and V_2 denote respectively initial, intermediate, and final volumes, then

$$P_1 V_1 = P_2 V_2 \tag{44}$$

and

$$P_1 V_1^\gamma = P_0 V_0^\gamma \tag{45}$$

It also follows that $V_0 = V_2$ since no gas was lost between the intermediate and final states. Hence,

$$\left(\frac{P_2}{P_1}\right)^\gamma = \left(\frac{V_1}{V_2}\right)^\gamma = \frac{P_0}{P_1} \tag{46}$$

By taking the logarithm of the first and last members this becomes

$$\gamma = \frac{\log P_0 - \log P_1}{\log P_2 - \log P_1} \tag{47}$$

Writing $P_1 = P_0 + h_1$ and $P_2 = P_0 + h_2$ and making use of the fact that $\log (1 + \delta)$, where δ is any quantity small compared to unity, may be written as $k\delta$, equation 47 becomes

$$\gamma = \frac{\log\left(1 - \dfrac{h_1}{P_0 + h_1}\right)}{\log\left(1 - \dfrac{h_1 - h_2}{P_0 + h_1}\right)} = \frac{h_1}{h_1 - h_2} \tag{48}$$

Thus γ is very simply obtained, and it is observed that the kind of liquid in the manometer, or the scale units in which the level differences h_1 and h_0 are expressed, are unimportant provided they are uniform.

In practice, the time of tapping the valve influences the result. If this is too short the pressure may not be allowed to reach the atmospheric value; and if too long, thermal equilibrium may in part take place while the valve is open.

γ by the Method of Jamin and Richard. If in any way the specific heat of a gas under constant pressure and that under constant volume are independently determined, then of course $\gamma(=C_p/C_v)$ may be at once expressed.

Jamin and Richard[25] have reported results obtained in which these quantities were expressed quite simply. Using a definite mass M of gas in a container at an initial temperature T_0, a certain quantity of heat ΔQ was added. In the first case the gas was maintained under the condition of constant pressure and its temperature was raised to a value T_1. Then the same amount of heat ΔQ was added when the same quantity of gas under the same initial conditions was limited to a constant volume and the temperature raised to T_2. Thus:

$$\Delta Q = MC_p(T_1 - T_0) = MC_v(T_2 - T_0) \tag{49}$$

and

$$\gamma = \frac{C_p}{C_v} = \frac{T_2 - T_0}{T_1 - T_0} \tag{50}$$

These changes in temperature were measured by a manometer attached to the flask containing the gas. In practice, the thermal capacity of the container is so great that it is apt to completely mask the effect of the contained gas whose thermal capacity is relatively very small.

γ by the Method of Oscillatory Compression of the Gas. A qualitative determination of the ratio of the specific heats of a gas may be obtained from a very simple experimental arrangement first described by Rüchardt.[26] A large container filled with the gas under investigation is provided at the top with a vertical glass tube of extremely uniform bore. A steel ball of mass M fitting perfectly in the bore of the tube is dropped and because of the nice fit it compresses the gas and oscillates up and down with a definite period T. Since a mechanical fit of this sort is not easy to procure, it has been found satisfactory in this laboratory to use a connecting U tube, containing a column of mercury which when displaced will oscillate back and forth. The period of a mechanical oscillator is expressed as

$$T = 2\pi\sqrt{\frac{M}{F_x/x}} \tag{51}$$

where M is the mass of the vibrating system, F_x/x is the spring factor, that is, the force F_x acting at the displacement x divided by the displacement. For a compression of the gas due to a displacement of the mercury of x, the restoring force will be due in part to a head of mercury of $2x$, and to the adiabatically compressed gas. The total force is then $2x\,dgA + \Delta P \cdot A$ where A is the sectional area of the uniform tube, d is the density of mercury, g is the acceleration due to gravity, and ΔP is the increase in pressure for the displacement x. To evaluate ΔP the adiabatic relationship $PV^{\gamma} = C$ is differentiated, giving

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[25] J. Jamin and F. Richard, *Compt. rend.*, **71**, 336 (1870).

[26] E. Rüchardt, *Phys. Zeit.*, **30**, 57 (1929).

$$V^{\gamma}\,\Delta P + \gamma\,PV^{\gamma-1}\,\Delta V = 0 \tag{52}$$

so that

$$\Delta P = \frac{-\gamma P}{V}\,\Delta V \tag{53}$$

and ΔV is A times x. Hence in equation 51 the spring factor is

$$\frac{F_x}{x} = \frac{2x\,gAd + A \cdot \Delta P}{x} = 2A\,dg - \frac{\gamma A^2 P}{V} \tag{54}$$

This may be solved explicitly for γ on introducing the period T from equation 51, giving

$$\gamma = \frac{V}{A^2P}\left(2A\,dg - \frac{4\pi^2 M}{T^2}\right) \tag{55}$$

In practice there is a constant frictional force that may be introduced in equation 54 and ultimately eliminated by noting the period T_0 of the mercury when the volume is not closed so as to be subject to adiabatic compression.

γ by the Method of Velocity of Sound. When a sound wave passes through a gas, the velocity of propagation (V) was shown by Laplace to be given by the expression

$$V = \sqrt{\frac{C_p}{C_v} \cdot \frac{P}{\rho}} \tag{56}$$

where P is the pressure of the gas and ρ its density.

That the value of γ should enter in this expression will be shown later, see equation 48, in Chapter VIII. Since the velocity, or more generally the wavelength of the sound wave is readily found experimentally as well as the pressure and density of the gas, then the value of γ may be determined. This method has been employed by numerous investigators. As originally employed by Kundt,[27] the gas in a hollow tube was set in resonance by a vibrating rod with which it was in contact. By observing dust figures in the resonating column of gas the length of the tube could be adjusted to include a whole number of half wavelengths. The distance between nodes, shown by the patterns of dust, gave directly the half wavelength $\lambda/2$. The frequency

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[27] A. Kundt, *Ann. Physik*, **127**, 497 (1866).

n was calculated from the length of the sounding rod. The velocity was then given by the product $n\lambda$. Kundt and Warburg[28] used an improved form of the apparatus to study the velocity of sound in mercury vapor. Many subsequent investigations,[29] in which this apparatus in modified form has been employed, have been carried out. Keesom and van Itterbeek[30] have measured the velocity of sound in helium gas at a temperature of 4° K.

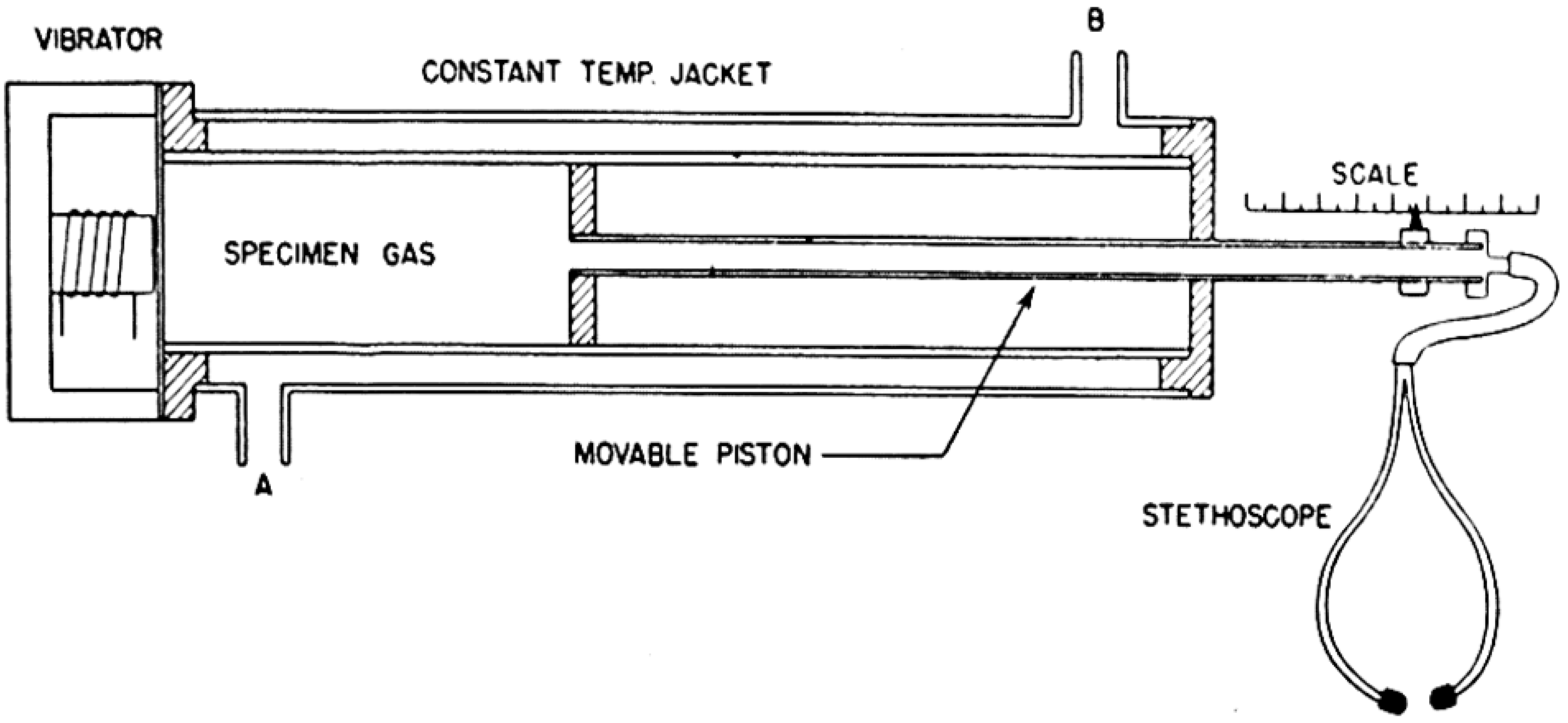

FIG. 32. Apparatus for the determination of the velocity of sound and hence the value of the ratio of specific heats of a gas.

A convenient form of apparatus for laboratory use is shown in Fig. 32. The cylindrical tube containing the specimen is surrounded by a jacket through which may be circulated cold water or steam giving the desired temperature. At the fixed end of the gas column is a vibrator (such as a telephone receiver) driven by the output of an audio oscillator of known frequency. A movable piston closes the other end of the tube and communicates with a stethoscope so that positions of the piston for maximum loudness can be determined. The half wavelength of the sound wave is thus found from the average difference between successive antinodes. The experiment can be repeated with various gases at different temperatures.

The Specific Heat of Gases at High Temperatures. At ordinary temperatures the specific heat of gases under constant pressure C_p is determined usually by the method of continuous flow. By this method the gas is made to pass at a uniform velocity through a thermally insulated chamber to which electrical power is supplied at a constant rate. If ρ is the density of the gas, dV/dt the volume flowing per second, C_p

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[28] A. Kundt and E. Warburg, *Ann. Physik*, **157**, 353 (1876).

[29] A. W. Witkowski, *Bull. Acad. Sci. Cracovie*, March, 1899; T. C. Hebb, *Phys. Rev.*, **14**, 44 (1919); J. R. Partington and W. G. Shilling, *Phil. Mag.*, **45**, 416 (1923).

[30] W. H. Keesom and A. van Itterbeek, *Comm.* 213B *Phys. Lab. Leiden* (1931).

the specific heat under constant pressure, and ΔT the rise in temperature of the gas on passing through the heated chamber, then,

$$\frac{EI}{J} = \rho \cdot C_p \cdot \frac{dV}{dt} \cdot \Delta T \pm \text{Losses} \tag{57}$$

where $(EI)/J$ is the electrical power supplied, expressed in calories per second.

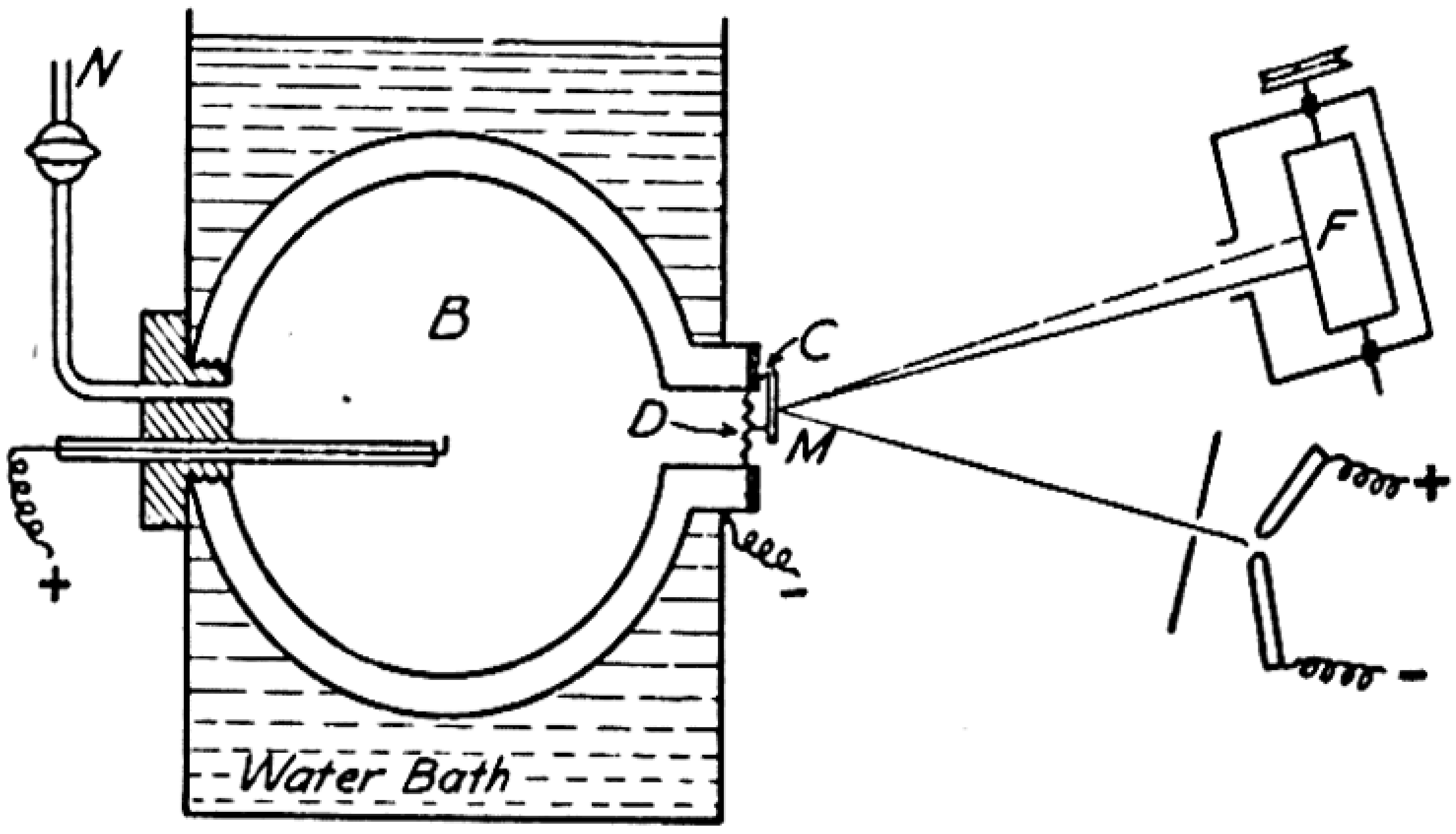

FIG. 33. Apparatus of Pier for determining the specific heat of a gas at high temperatures.

At high temperatures various other forms of apparatus have been employed to determine the specific heat. The arrangement shown in Fig. 33 as used by Pier[31] is typical of that used by several other investigators. This consisted of a bulb-shaped bomb B in which was exploded mixtures of the gases under investigation. Thus, for example, for hydrogen and chlorine, the proper amounts of each to combine forming HCl were placed in the bomb and exploded. The change in pressure within the bomb was communicated through the diaphragm D to the mirror M causing it to rotate. This rotation altered the position of a reflected spot of light on the moving film F. The experiment was next repeated using first an excess of hydrogen, then again using an excess of chlorine. Differences in the resulting pressures in these cases allowed the calculation of the specific heats of the two gases at temperatures as high as 2,000° C.

It is a fact that most available data on the specific heats of gases at high temperatures have been shown by theoretical considerations to be badly in error. An investigation was carried out at Cambridge using a quite different method.[32] In this procedure a stream of the gas under investigation was made to pass through a tube along which a definite gradient in temperature had been established. From the change in the distribution of temperature due to the flow of gas it was possible to make a direct calculation of the specific heat of the gas.

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[31] M. Pier, *Zeit. Electrochem.*, **15**, 536 (1909); *see also* N. Bjerrum, *Zeit. Electrochem.*, **18**, 101 (1912).

[32] P. M. S. Blackett, P. S. H. Henry, and E. K. Rideal, *Roy. Soc. Proc.*, **126**, 319 (1930).

Theoretical. *Classical Value of C_v for Gases.* The specific heat of a substance under constant volume expressed in differential form is

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v \tag{58}$$

It was seen in equation 22 that for a mass point gas the only way of storing energy was in the form of increased kinetic energy of the particles. To that motion three degrees of freedom were assigned, and the total kinetic energy per gram-mole was equal to $\frac{3}{2}RT$, where R represents the universal gas constant and T the absolute temperature.

Hence it should be expected that for a gram-mole of a monatomic gas

$$C_v = \frac{\partial(\frac{3}{2}RT)}{\partial T} = \frac{3}{2}R = 2.98\,\frac{\text{calories}}{\text{gm-mol. deg.}} \tag{59}$$

In practice the specific heat under constant pressure C_p is the quantity that is usually obtained, and this may be changed to C_v by the relationship of equation 21:

$$C_v = C_p - R \tag{60}$$

For a diatomic gas, at temperatures not too high, a value of γ (1.403) (see page 55) is obtained, which indicates the existence of five degrees of freedom. Hence from the equipartition principle for diatomic gases

$$C_v = \frac{\partial(\frac{5}{2}RT)}{\partial T} = \frac{5}{2}R = 4.97\,\frac{\text{calories}}{\text{gm-mol. deg.}} \tag{61}$$

In general, for f degrees of freedom

$$C_v = f\cdot\frac{R}{2} = 0.993f \tag{62}$$

Table 2 shows in a collective way the agreement between theoretical and experimental values for certain gases at ordinary temperatures.

Variation of Specific Heat of Gases with Temperature. Eucken[33] has investigated the specific heat of hydrogen at temperatures as low as

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[33] A. Eucken, *Verh. deut. phys. Ges.*, **18**, 4 (1916).

20° K. using an electrical method. At low temperatures the number of degrees of freedom seemed to decrease, so that below 60° K. it acted like a monatomic gas with three degrees of freedom. Below 20° K. the specific heat fell even below that to be expected for an ideal monatomic gas. In this condition the substance is in the liquid phase.

At high temperatures the specific heats of all gases increase beyond their ideal classical values. Thus at 2,000° C. Pier found for Cl a value for C_v of 6.7 $\frac{\text{calories}}{\text{gm-mol. deg. C.}}$ and for hydrogen at the same temperature the value 5.8 $\frac{\text{calories}}{\text{gm-mol. deg. C.}}$.

TABLE 2

Theoretical and Experimental Values for the Specific Heat under Constant Volume and the Ratio of the Specific Heats for Certain Gases

Gas	Atoms per Molecule	Degrees of Freedom	$C_v \frac{\text{calories}}{\text{gm-mol. deg. C.}}$ Theoretical	C_v Experimental	γ Theoretical	γ Experimental
Argon	1	3	2.98	2.98	1.66	1.66
Helium		3		2.98		1.66
Air	2	5	4.97	4.95	1.400	1.403
Oxygen		5		5.04		1.396
Nitrogen		5		4.93		1.405
Carbon monoxide		5		4.94		1.404
Methane	3	6 or more	>5.96	6.48	<1.33	1.31
Carbon dioxide				6.75		1.302
Nitrous oxide				6.81		1.300

It is thus apparent that any satisfactory expression for the specific heat of a gas must be dependent on the temperature. It must contain a function of the temperature which will lead to a larger value of C_v at high temperatures and go to zero at the absolute zero.

Classical Value of C_v for Solids. In the solid state it is assumed that each particle is limited in its domain of travel. It can oscillate in three dimensions about a fixed point of the lattice, as a center. Because of this linear three-dimensional motion, classical theory would assign three degrees of freedom, and the kinetic energy per gram-mole would be given by the expression $\frac{3}{2}RT$. But this is not all, for since the motion is vibratory in nature there must be an average amount of potential energy just equal to the time average of the kinetic energy. Together there are therefore six degrees of freedom, and the molecular specific heat under constant volume becomes

$$C_v = \frac{\partial(\frac{6}{2}RT)}{\partial T} = 3R = 3(1.986) = 5.96 \frac{\text{calories}}{\text{gm-mol. deg. C.}} \tag{63}$$

Dulong and Petit[34] had observed that the experimental value of the specific heat of some twenty common metals when multiplied by their atomic weight gave approximately a constant value of 6.4. This is, of course, the specific heat under constant pressure, and from it C_v may be found. The development of this relationship involving the difference of the specific heats in solids is found in Chapter VIII, page 251. If α denotes the coefficient of linear expansion, V the volume per gram-mole, ϵ the coefficient of volume elasticity or bulk modulus, T the absolute temperature, and J the mechanical equivalent of heat, then,

$$C_v = C_p - \frac{9\alpha^2\epsilon VT}{J} \tag{64}$$

Nernst and Lindemann,[35] by allowing for the condition existing at the melting point and the fact that C_p varies as α, concluded that this quantity is expressible as

$$C_p - C_v = 0.0214\,\frac{C_p^2 T}{T_m} \tag{65}$$

where T_m denotes the melting temperature.

Several substances, such as boron, carbon, and silicon, show values of specific heat at ordinary temperatures which violate the Dulong and Petit rule. It will be seen that this is as might be expected according to more complete theories of specific heat.

Variation of C_v of Solids with Temperature. The results of investigators very early revealed the fact that only at ordinary temperatures was the conclusion of Dulong and Petit valid even for the simple metals. At low temperatures a decided falling off in C_v was observed, indicating that at the absolute zero the value of C_v would be zero. Again at high temperatures the specific heat increased substantially above the ideal value. It was further observed that, in those substances for which the value of C_v was below the ideal limit at ordinary temperatures, a sufficient increase in temperature brought the specific heat up to the Dulong and Petit value. Thus if the temperature scale be suitably altered the temperature-specific heat relationship for all substances is about the same.

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[34] P. L. Dulong and A. T. Petit, *Ann. chim. phys.*, **10**, 305 (1819).

[35] W. Nernst and F. A. Lindemann, *Zeit. Electrochem.*, **17**, 817 (1911).

Figure 34 represents the variation in C_v with temperature for the three substances lead, silver, and diamond. This shows that whereas lead has attained the ideal value at −100° C., diamond yields a value still too small at 1,000° C. It is here also apparent that the classical expression for the atomic heat of solids, equation 63, is insufficient to represent the complete facts. A satisfactory expression for C_v must involve T and also some characteristic property of the material. Schrödinger[36] has shown that if this arbitrary property characteristic of each substance be denoted by θ and if T be the temperature of the substance, then there is some function (F) of T/θ the same for all substances which will completely represent the value of C_v. Thus if a complete curve is known for any one substance, and the specific heat of any other substance known at one temperature, it is possible to determine the θ for the second substance. Knowing θ, then, the complete curve for the variation in the specific heat of that substance with temperature can be deduced for all except very high temperatures. Schrödinger found that those substances belonging to the cubic crys-

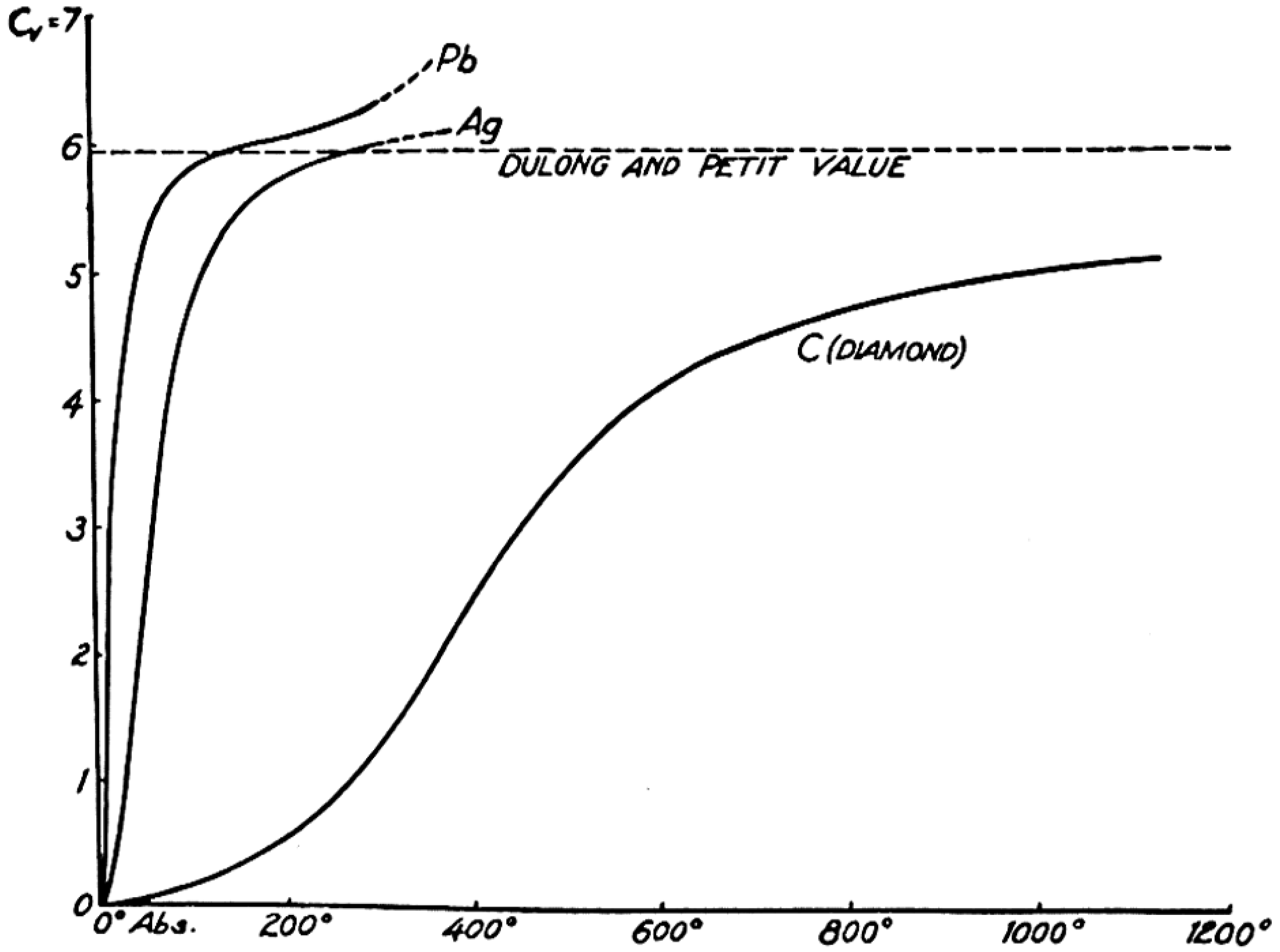

FIG. 34. Variation in atomic heat with temperature for lead, silver, and diamond.

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[36] E. Schrödinger, *Phys. Zeit.*, **20**, 452 (1919).

talline system, whether it be simple cubic like NaCl, face-centered like all ductile metals, body-centered like iron, or the diamond-type lattice, agree particularly well. Those materials crystallizing in other systems seemed to exhibit specific heats falling off at low temperatures according to a different law.

Einstein's Theory of Specific Heats. The first development for the specific heat of a substance showing approximately the proper dependence upon temperature was due to Einstein.[37]

It had already been shown by Planck that the methods of classical statistics resulted in a wrong law in the field of radiation. Einstein assumed that, also, in the field of atomic heats, classical theory (particularly the ideas of total degrees of freedom and equipartition of energy) was inadequate. In the development of Planck on the basis of the quantum theory an expression had already been formulated for the average energy $\bar{U}$ of a linear oscillator in one direction having the frequency ν and the temperature T. For a discussion of this expression see page 161. This is

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1} \tag{66}$$

where k denotes the gas constant per molecule, h the Planck constant, T the absolute temperature, and e the base of Naperian logarithms.

If the solid be considered (substantiated by x-ray diffraction experiments) as made up of an orderly placement of particles, in which each particle may vibrate with respect to a fixed point of the lattice in three-dimensional space, then this expression for the average energy is directly applicable. Since at any instant a given particle may be undergoing motion in three independent, mutually perpendicular directions, simultaneously, Einstein expressed the complete average energy per particle as three times Planck's value. Then, if it be assumed that the total number of particles N in a gram-mole have identical frequencies, this quantity N would also appear as a factor in the expression for the total energy. A common frequency might be expected to exist as a first approximation in isotropic crystalline substances since the force field about any atom due to its neighbors would approximate that about any other particle.

Hence the total energy Q of the N particles is

$$Q = 3N \cdot \frac{h\nu}{e^{h\nu/kT} - 1} \tag{67}$$

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[37] A. Einstein, *Ann. Physik*, **22**, 800 (1907); **35**, 683 (1911).

and

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v = 3Nk \cdot \frac{x^2 e^x}{(e^x - 1)^2} \qquad (68)$$

where x is written for $h\nu/kT$.

For x approaching infinity, that is, ν very large or T very small: $C_v \rightarrow 3R \cdot 0 \rightarrow 0$.

For x approaching zero, that is, ν very small or T very large; $C_v \rightarrow 3R$.

Thus we see that at very low temperatures this expression agrees with the observed experimental results in indicating a lower value of C_v. The upper limit of this expression at high temperatures is the usual Dulong and Petit value. Further it may be observed that different substances might be expected to have different values of C_v at the same temperature, if the ν characteristic of each were different. The larger ν the less is the value of C_v, other things being equal.

INTERPRETATION OF THE FREQUENCY ν

The frequency ν is the only unknown quantity in the formula of Einstein. This may be determined in the several following independent ways:

(*a*) *Experimental.* For a particular substance at a definite temperature, one may substitute in equation 68 the value of the specific heat in fundamental units at that temperature. The equation may then be solved for ν. In this way one could readily determine the frequency characteristic of any substance for which C_v is known.

(*b*) *Elastic Properties.* If each atom is thought of as vibrating in a force field due to its neighbors, then, as in any mechanical oscillator, the greater the mass moving (atomic weight) the greater the period or the less the frequency. The spring factor may be thought of as due to the force of interaction between neighboring portions of the lattice and is thus revealed by the compressibility of the substance. If a substance is not readily compressed, or in other words if it possesses a large value for its coefficient of volume elasticity, then the spring factor is large, the period of vibration small, or the frequency large. Considerations of this nature enabled Einstein to express the frequency as

$$\nu = 2.8 \times 10^7 \frac{\epsilon^{1/2}}{A^{1/3} \rho^{1/6}} \text{ per second} \qquad (69)$$

where ϵ denotes the bulk modulus or coefficient of volume elasticity, A the atomic weight, and ρ the density of the substance.

(*c*) *Melting-Point Method.* From the assumptions that, at the melting point, the amplitude of vibration of a particle is of the order of the distance between particles in the crystal lattice, Lindemann[38] was able to express the frequency ν in a form involving the melting point. Temperature is brought into the energy expression by first getting an expression for the kinetic energy of the oscillator classically and equating it to $\frac{3}{2}kT$. The final expression is of the form

$$\nu = 2.8 \times 10^{12}\, T_m^{1/2} A^{-5/6} \rho^{1/3} \text{ per second} \tag{70}$$

where T_m is the melting point of the substance in degrees absolute, A is its atomic weight, and ρ is its density. It is thus evident that a substance with a high melting point (diamond, etc.) is also one with a large characteristic frequency, and hence one of low value of C_v at ordinary temperature.

(*d*) *Reststrahlen.* If the particles of a substance are characterized by a definite frequency ν, then classically they will absorb most strongly radiation of this same frequency. The vibrating particles, on the other hand, will reradiate this frequency most strongly. Thus if the cleavage surface of a natural crystal is exposed to white radiation, then, in the reflected beam, the characteristic frequency ν will predominate. Rubens and Nichols,[39] using surfaces of metallic halide crystals, were the first to show the effect experimentally. Continuous radiation after five successive reflections, as shown in Fig. 35, resulted in a reflected beam having a decided maximum of energy at a particular frequency. These residual frequencies, termed "Reststrahlen," have been determined for many substances. More recent experiments[40] show that the "Reststrahlen" are really more complicated. Instead of the single important frequency, there are many other frequencies, some of the peaks displaying a resolvable fine structure.

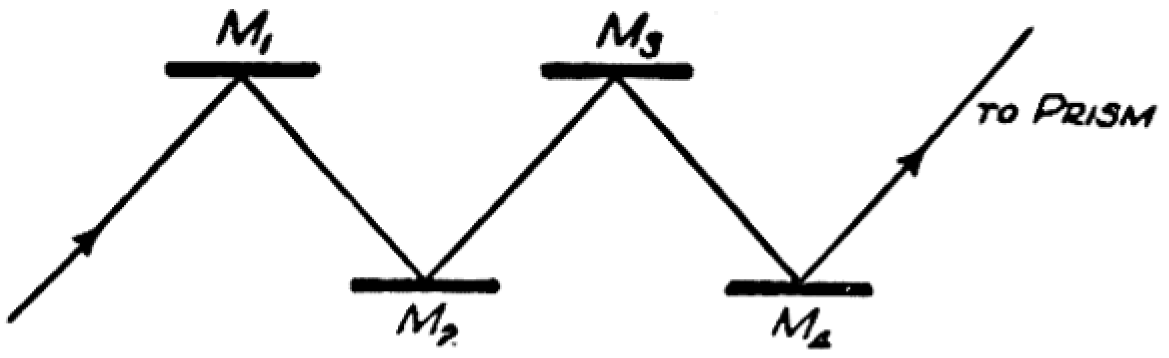

FIG. 35. Successive reflections to yield residual rays (Reststrahlen).

In Table 3 are collected the data on ν for a few materials, obtained by the various methods just described. The procedure employed is shown by the lettering at the heading of each column. Although the agreement for the different methods is not exact, it is very significant that they are of the same order of magnitude.

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[38] F. A. Lindemann, *Phys. Zeit.*, **11**, 609 (1910).

[39] H. Rubens and E. F. Nichols, *Weid. Ann.*, **60**, 418 (1897).

[40] H. Rubens and H. Wartenburg, *Ber. kgl. preuss. Akad. Wiss.*, p. 169, 1914; C. E. Blom, *Ann. Physik*, **42**, 1397, 1913.

From a formula developed by Lindemann[41] calculations were made[42] of the frequencies characteristic of most of the pure elements. These values of γ when plotted against atomic number show an interesting periodicity. This distribution with respect to atomic number is shown in Fig. 36. It may be observed that at the peaks of the curve are those elements with four electrons in the outer shell, instead of those with one electron as characterizes the elements at the peaks in the curve for atomic volumes.

TABLE 3

FREQUENCY CHARACTERISTIC OF THE LATTICE PARTICLE

All values to be multiplied by 10^{12} per sec.

Substance	Method			
	(*a*)	(*b*)	(*c*)	(*d*)
Al	8.3	6.7	7.6	...
Cu	6.7	5.7	6.8	...
M	4.8	....	4.4	...
Ag	4.5	4.1	4.4	...
Pb	1.5	2.2	1.8	...
Diamond	40.0	32.5	...	...
NaCl	5.9	....	7.2	5.8
KCl	4.5	....	5.6	4.7

Nernst-Lindemann Theory. The first comparisons of the experimental values of specific heats with those computed from the Einstein formula were very encouraging. However, upon more exact examination, using the specific heat measurements of Nernst, at low temperatures discrepancies between theory and experiment were apparent. The observed values of the atomic heat fell off with decreasing temperature more slowly than the values predicted by the Einstein formula (adjusted to be correct at moderate temperatures). To obtain a better agreement a rather empirical formula was proposed by Nernst and Lindemann.[43] In the sense that the radiation from an oscillator (not purely harmonic) is observed to consist of a fundamental frequency

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[41] F. A. Lindemann, *Ber. deut. phys. Ges.*, **13**, 1107 (1911).

[42] W. Biltz, *Zeit. Electrochem.*, **17**, 676 (1911).

[43] W. Nernst and F. A. Lindemann, *Zeit. Electrochem.*, **17**, 817 (1911).

ν, together with overtones whose frequencies are integral multiples of ν, it was proposed that the energy resident in the atomic oscillator might be regarded as in part associated with the fundamental frequency, and in part in the overtone frequencies. As a first approximation only the first overtone was considered, and it was assumed that the energy was on the average equally divided between the fundamental frequency ν and this first overtone of frequency 2ν. Following the development used for equation 68 one thus obtains

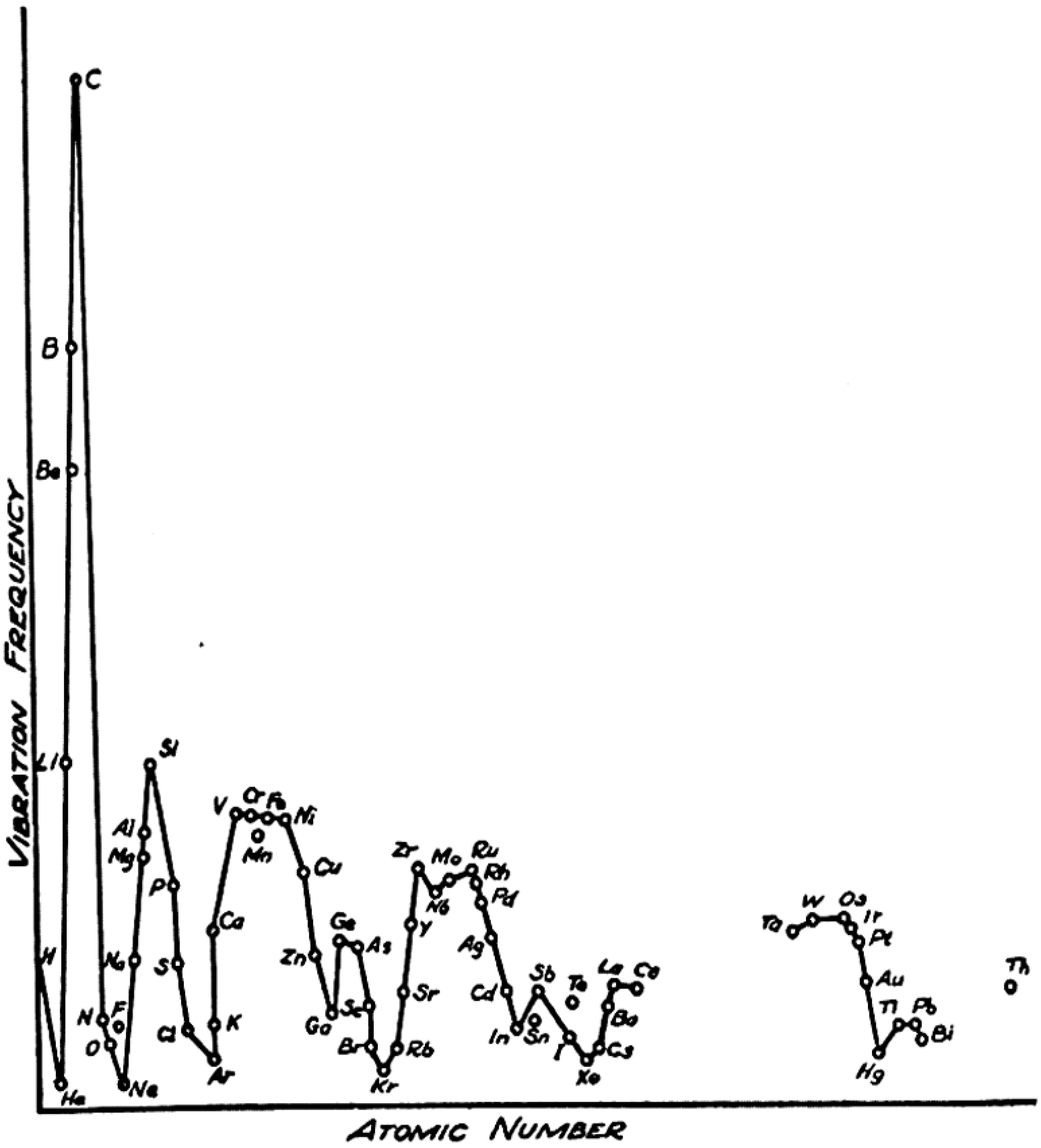

FIG. 36. Atomic number and calculated characteristic frequencies.

$$C_v = \tfrac{3}{2}kN\left[\frac{x^2e^x}{(e^x-1)^2} + \frac{y^2e^y}{(e^y-1)^2}\right] \tag{71}$$

where $x = h\nu/kT$ and $y = (2h\nu)/kT$.

The assumptions in this development are so arbitrary that the final formula must be considered as purely empirical, and naturally, since it involves two constants, it should allow for better agreement between experimental and expected values. It is undoubtedly a step in the right direction, however, in overthrowing the assumption of a single definite identical frequency for all of the particles of the lattice. When one considers that the frequency of any atom is determined by the force field due to its neighboring atoms then one must conclude that no two atoms would at the same instant necessarily have the same frequency. A type of Maxwellian distribution might be expected to apply to the frequencies of the particles.

Debye Theory. Since the publication of the Einstein equation a great number of theories of specific heats have been proposed. One of the most successful theories has been that due to P. Debye.[44] It had been shown by Weber that for N independent particles a number of frequencies up to $3N$ is possible. Now if the expression of Planck for the energy associated with any particular frequency ν be maintained, the total energy Q is expressed as

$$Q = \sum_{\nu=0}^{\nu=3N} \frac{h\nu}{e^{h\nu/kT} - 1} \tag{72}$$

By considering the matter as a continuum in which the propagation velocity of a longitudinal wave is represented by v_L and that of a transverse wave by v_T, Debye postulated the existence of elastic frequencies distributed in value in a continuous manner. By assuming that there are in all $3N$ such elastic frequencies and that arbitrarily there is in any particular substance no frequency greater than a certain maximum value ν_m, Debye showed that equation 72 for the total energy might be written as

$$\begin{aligned} Q &= 4\pi V\left[\frac{1}{v_L} + \frac{2}{v_T}\right]\int_0^{\nu_m} \frac{h\nu}{e^{h\nu/kt} - 1} \cdot \nu^2 \cdot d\nu \\ &= \frac{9Nh}{\nu_m^3}\int_0^{\nu_m} \frac{\nu^3 \cdot d\nu}{e^{h\nu/kT} - 1} \end{aligned} \tag{73}$$

In this equation, V is the volume per gram-mole. Since $h\nu/kT$ has the dimensions of a pure number, $h\nu/k$ may be regarded as a temperature. The particular value of this expression when ν has the value ν_m is called by Debye the characteristic temperature of the substance (θ). The differentiation of equation 73 with respect to T gives:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{9N}{\nu_m^3}\int_0^{\nu_m} \frac{\frac{h^2\nu^4}{kT^2} \cdot e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \cdot d\nu \tag{74}$$

Writing x for $h\nu/kT$ and changing the limits of integration by introducing $d\nu = (kT/h) \cdot dx$, equation 74 becomes

$$C_v = \frac{9Nk^4T^3}{h^3\nu_m^3} \cdot \int_0^{\nu_m \cdot x/\nu} \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx \tag{75}$$

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[44] P. Debye, *Ann. Physik*, **39, 789 (1912).**

When partially integrated this becomes

$$C_v = 9Nk\left[\frac{4k^3T^3}{h^3\nu_m^3}\int_0^{\nu_m \cdot x/\nu}\frac{x^3dx}{e^x - 1} - \frac{x^4}{e^x - 1}\right]$$

$$= 9R\left[4\frac{T^3}{\theta^3}\int_0^{\theta/T}\frac{x^3}{e^x - 1}\cdot dx - \frac{x^4}{e^x - 1}\right] \qquad (76)$$

The definite integral in equation 76 may be evaluated numerically for any particular value of θ/T. From this, C_v may then be found. Debye tabulated this complete value C_v for a range of θ/T from 0 to 30 in tenths. The quantity characteristic of a particular substance is thus its value of θ. These characteristic temperatures for a few common substances are given in Table 4.

TABLE 4

CHARACTERISTIC TEMPERATURES $\theta = h\nu_m/k$ FOR SOME COMMON SUBSTANCES

Substance	θ	Substance	θ
Pb	88	Zn	235
Hg	97	NaCl	281
Cd	168	Cu	315
Na	172	Al	398
Ag	215	Fe	453
KCl	230	Diamond	1860

The variation between the value for lead and that for diamond is of the same order as the variation in their melting points. When applied to existing experimental data the Debye expression has proved to be very successful in representing the actual variation with temperature.

When T is very small (that is, x very large), then the second term of the bracket in equation 76 becomes negligible in comparison with the first term. The limiting value of the integral under this same condition may be shown by expansion in series form to be $\pi^4/15$.

Thus it follows that

$$\to C_v \ \frac{12}{5}\frac{\pi^4 R}{\theta^3}\cdot T^3 \quad \text{as} \quad T \to 0 \qquad (77)$$

or at very low temperatures

$$C_v = A \cdot T^3 \qquad (78)$$

where A is a constant.

A statement to this effect, that at low temperatures the specific heat of all substances varies as the cube of the absolute temperature of the substance, is known as Debye's law. For values of T not greater than $(\theta/12)$ it is found to represent observed data with an error less than 1 per cent.

The atomic specific heats C_v of copper and of platinum have been measured[45] at temperatures between 1° K. and 20° K. The values are found to be well represented by the following equation

$$C_v = D\left(\frac{T}{\theta}\right) + BT \tag{79}$$

The term $D(T/\theta)$ is a Debye function of the characteristic temperature θ at the Kelvin temperature T, and B is a constant for a particular metal. For platinum $D(T/\theta)$ is numerically expressible as $464.4(T/\theta)^3$. The values of θ and B are empirically determined to be as follows: for copper, 335 and 0.0001777, and for platinum, 233 and 0.001607, respectively.

At very high temperatures x is very small so e^x may be replaced by 1 and $(e^x - 1)$ by x. Equation 70 then reduces to

$$C_v = 9R \cdot \frac{T^3}{\theta^3} \int^{\theta/T} \frac{x^4}{x^2} \cdot dx = 9R \cdot \frac{T^3}{\theta^3} \cdot \frac{\theta^3}{3T^3} = 3R \text{ (approx.)} \tag{80}$$

thus approximating the classical value.

Other Theories. Many other developments for the variation of specific heat with temperature have been proposed. Among these may be mentioned the investigation of Born and Kármân,[46] who developed an expression for the specific heat of crystalline compounds. A simple cubic lattice of the rock salt type may be regarded as two interpenetrating face-centered lattices, one comprising negative chlorine ions and the other the positive sodium ions. Now an electric wave incident upon this crystal would at the same instant give forces in opposite directions upon the two lattices, owing to their unlike charges, so that one system would vibrate as a whole with respect to any other penetrating lattice. In addition to frequencies of this sort, any one point might possess Debye frequencies with respect to other similar points in its own lattice. In general for a substance consisting of S interpenetrating lattices the expression for the specific heat under constant volume was developed to have the form

$$C_v = \frac{1}{3S}\left[\sum_{i=1}^{i=3} D(x_i) + \sum_{i=4}^{i=3S} E(x_i)\right] \tag{81}$$

The first term in the bracket is a contribution of the Debye form, and the second is due to the monochromatic superimposed frequencies and has the form of the Einstein term. For pure substances (no interpenetration), this last term vanishes. Only in the region of very low temperatures and also very high temperatures has it been possible to carry out the required calculation for even very simple substances.

At very low temperatures equation 81 may be shown to approximate the following:

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[45] J. A. Kok and W. H. Keesom, *Physica*, **3**, 1035 (1936).

[46] M. Born and T. V. Kármán, *Phys. Zeit.*, **13**, 297 (1912); M. Born, *Atomictheorie des festes Zustandes*, Teubner, Leipzig, 1923; see also C. V. Raman, *Proc. Ind. Acad. Sci.*, **A14**, 459 (1941).

$$C_v = \frac{16}{5} \cdot \pi^5 \cdot \frac{k^4}{h^3} \cdot V_A \cdot \frac{T^3}{q^3} \tag{82}$$

where V_A represents the volume occupied by a gram-mole of the substance, k the gas constant per molecule, h the Planck constant, and q is a mean acoustic velocity. If q be regarded as independent of the temperature, then again the third-power law of Debye at low temperature is observed.

Molecular Spectra and Specific Heats. The importance of a correct theory of specific heat lies in the fact that it must necessarily reveal information regarding the ultimate motions of the constituent particles of a substance. Another powerful source of information regarding these ultimate motions has now come to be a study of the frequencies, particularly those of absorption in the infrared region, characteristic of the substance. It had been observed that, if continuous radiation were passed through an absorbing cell containing a gas, certain frequencies were almost completely absorbed. The form of these absorption curves as originally observed in diatomic gases is shown in Fig. 37 plotted on a frequency scale. Now as the temperature of the absorbing gas was increased the two absorption peaks were observed to move farther apart. From a classical point of view this might have been explained as the superposition of two frequencies, one rather small on account of the rotation of the molecule ν_r and one large because of a vibration within the molecule ν_v. The result of these two would be two frequencies, one equal to the sum and one equal to the difference of the two fundamental frequencies ($\nu_v \pm \nu_r$). An increase in temperature producing an increased ν_r explained the observed separation of the peaks. This shift of the peaks in terms of wavelength, with changing temperature, was found to obey a law expressed by von Bahr[47] as

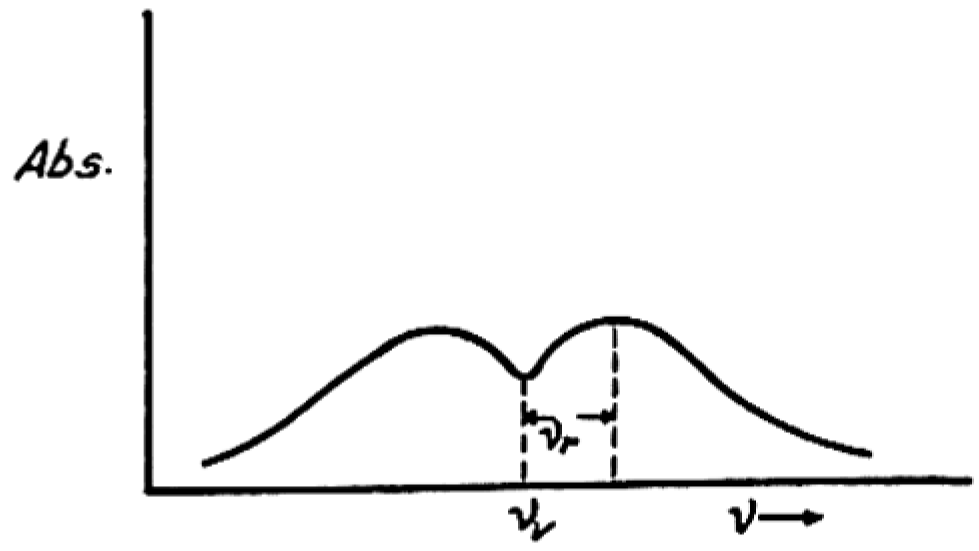

FIG. 37. Unresolved infrared absorption band, intensity of absorption plotted with frequency.

$$\frac{\lambda_1 \lambda_2}{\lambda_1 - \lambda_2} \sqrt{T} = c \text{ (Constant)} \tag{83}$$

In this expression λ_1 and λ_2 are the wavelengths, respectively, of the peaks at a wavelength greater and at a wavelength less than that of the center of the band, and T is the absolute temperature of the absorbing gas.

Using a spectrometer of greater resolving power it was shown by Paschen, von Bahr, and many others that these curves really possessed a fine structure. Figure 38 shows an intensity of absorption-wavelength curve of this sort obtained by Imes[48] for HCl vapor. It was at once observed that the shift of the peaks of Fig. 37, that was observed with increasing temperature did not mean any alteration in the wavelength of the fine structure peaks. The curve in Fig. 37 is the envelope of that shown in Fig. 38, and the observed shift in the position of the peaks was shown to be due simply to the displacement of the quality of maximum absorption of energy to more outlying wavelengths in the fine structure.

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[47] Eva von Bahr, *Ber. deut. phys. Ges.*, **15**, 710 (1913) *et seq.*

[48] E. Imes, *Astrophys. Jour.*, **50**, 251 (1919).

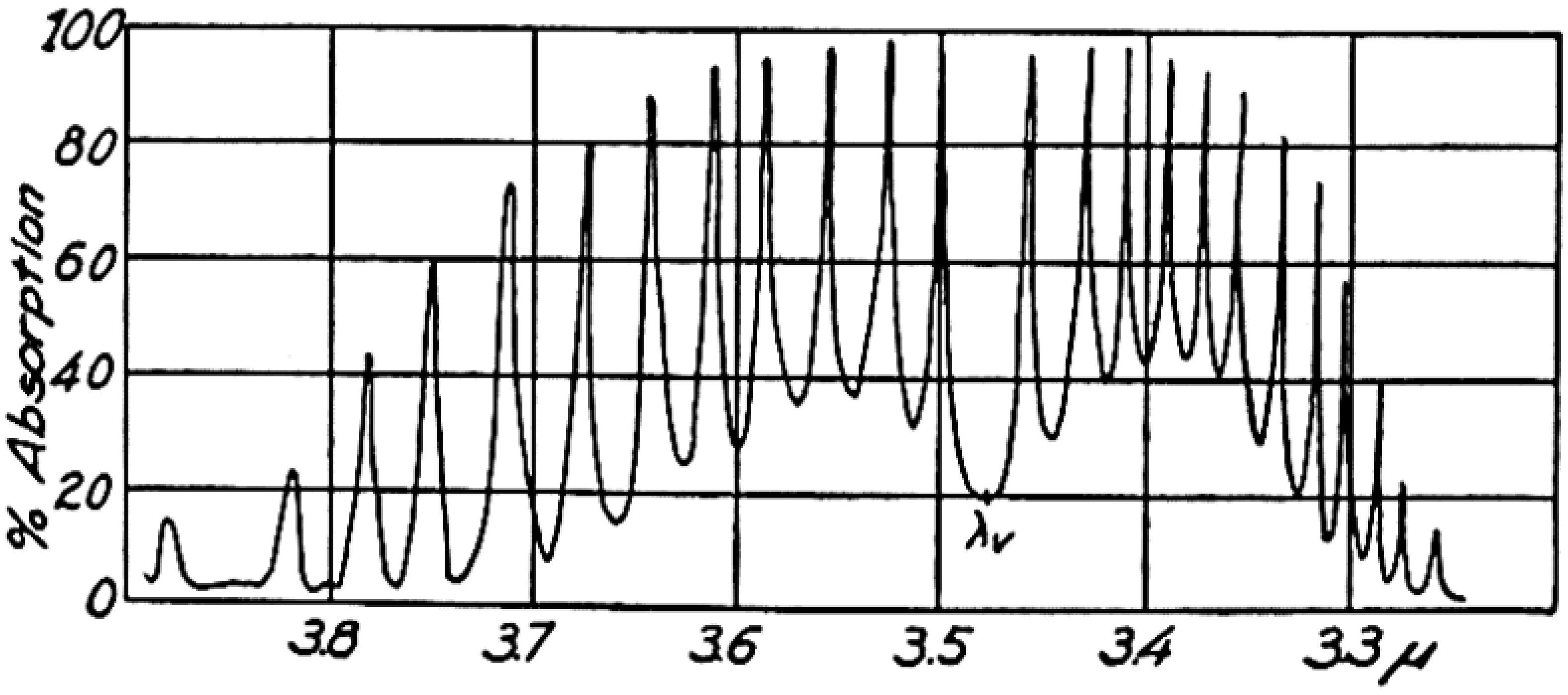

FIG. 38. Intensity of absorption for HCl plotted with wavelength (Imes).

The application of the quantum postulates of Bohr to the rotational and vibrational motions of the molecule can now explain this fine structure very satisfactorily. The wavelength peaks of Fig. 38, when transformed to a frequency scale, show as lines separated by a constant frequency interval. This is illustrated in Fig. 39. It must be remembered that the frequency absorbed by an oscillator is not necessarily the natural frequency of the oscillator (only in the limit of large quantum numbers — correspondence principle) but is determined by the difference in energy between the initial and final states of the oscillator. Thus, if W_{final} denote the energy of the system after absorption, W_{initial} the energy of the system in the beginning, and h the Planck constant, then the frequency of the radiation absorbed $\nu_{\text{abs.}}$ is given by the relationship

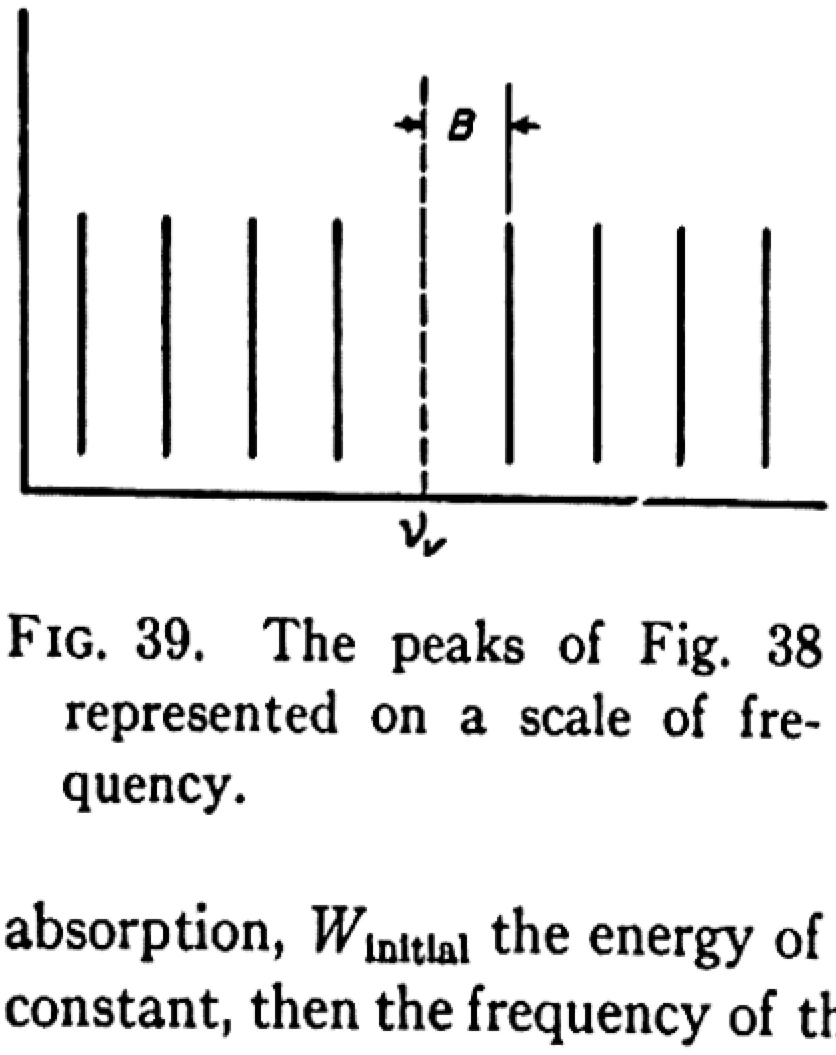

FIG. 39. The peaks of Fig. 38 represented on a scale of frequency.

$$W_{\text{final}} - W_{\text{initial}} = h\nu_{\text{abs.}} \tag{84}$$

It further follows from the quantization of momentum that if the vibrational or rotational states change they must do so always by definite increments. For rotation the increment of energy ΔE must be such that

$$\Delta E = \frac{Nh^2}{8\pi^2 I} \tag{85}$$

where h is the Planck universal constant and I is the moment of inertia of the particle for the particular axis under consideration. N is an integral number formed by taking $J(J+1)$ from $(J+\Delta J)(J+\Delta J+1)$ where J is the azimuthal quantum number (0, 1, 2, 3, etc.) and ΔJ is plus or minus one.

It follows that the whole band of Fig. 38 is associated with a definite jump in the vibrational quantum number such as from zero to one. If, while the vibrational energy is increasing, the rotational quantum number also increases by unity, then the total energy interchange is greater. Hence a definite higher frequency is absorbed according to the Bohr frequency postulate, giving thereby one of the fine structure lines at the right of the center, Fig. 39. However, it seems almost equally probable that in other molecules an increase in the vibrational quantum number is accompanied by a decrease in the rotational quantum number of one unit, giving one of the fine structure peaks at the left of the center in Fig. 39. The absence of a central peak means that a vibrational shift without a rotational shift is forbidden for this particular molecule. The various values of J in the initial state lead to the various fine structure peaks.

For a different vibrational quantum jump the whole absorption band is repeated at a different frequency. A detailed study of these absorption spectra has now been carried out for several substances. From the viewpoint of specific heats it is of interest to observe the complete absence of the " equipartition " principle in the individual processes.

Specific Heat of Hydrogen. The specific heat of hydrogen has received considerable attention both experimentally and theoretically. On the basis of wave mechanics an expression for the rotational atomic heat was developed by Hund.[49] Experiments by Eucken had indicated that at low temperatures hydrogen behaved as a monatomic gas. Thus classically the two rotational degrees of freedom had been suppressed. Now any expression yielding the rotational energy of the molecules as a function of the temperature will when differentiated with respect to T yield that part of the specific heat connected with rotation (C_r). The expression for C_r given by Hund follows.

$$C_r = R\sigma^2 \frac{d^2 \log Q}{d\sigma^2} \tag{86}$$

where R is the gas constant and σ has the value $(h^2/8\pi^2IkT)$. I is the moment of inertia of the molecule, k the gas constant per molecule, T is the absolute temperature, and h the Planck constant. The quantity Q, generally called the " Zustandsumme," is associated with the rotational energy and was expressed as

$$Q = \sum_{p=0}^{p=\infty} g_p e^{-p(p+1)\sigma} \tag{87}$$

in which p is a quantum number having successive integral values and g_p is the statistical weight of the pth quantum state and is given by $2p+1$. An equation of the form of 86 was first developed by Ehrenfest.[50]

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[49] F. Hund, *Zeit. Phys.* **42**, 93 (1927).

[50] P. Ehrenfest, *Verh. deut. phys. Ges.*, **11**, 451 (1913).

The result obtained by Hund for I, the moment of inertia of the hydrogen molecule, was only about one-third of that deduced by Hori[51] from a consideration of the ultraviolet band spectrum.

Heisenberg had successfully explained certain observations in the ultraviolet spectrum of helium by assuming that ordinary helium is a mixture of two forms. In one, the ortho form, the spin wave function of the two component electrons is regarded as antisymmetric in form; in the other, the para form, the electron spins are such as to yield a symmetric wave function.

On the basis of the results of Hori, Dennison[52] regarded ordinary hydrogen as a mixture of two distinct gases changeable one form into the other only in a very long time, compared to the time required for a determination of its specific heat. The distinction between the para and ortho forms was now based upon the combination of the nuclear spins of the two component atoms of the molecule, i.e., whether the nuclear spin wave functions are antisymmetric or symmetric.

It was now necessary to apply an equation similar to equation 86 to each of the two component states, symmetric and antisymmetric. For the symmetric states or para form of the gas, p takes successive even numbers whereas for the antisymmetric states or ortho form p assumes odd values. The total rotational specific heat C_r is thus the sum of two components C_s and C_a taken in the right proportion to represent the experimental data.

It thus follows that

$$C_s = R\sigma^2 \frac{d^2 \log Q_s}{d\sigma^2} \tag{88}$$

where

$$Q_s = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots \tag{89}$$

$$C_a = R\sigma^2 \frac{d^2 \log Q_a}{d\sigma^2} \tag{90}$$

where

$$Q_a = 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \cdots \tag{91}$$

and

$$C_r = \frac{\rho C_s + C_a}{1 + \rho} \tag{92}$$

where ρ denotes the number representing the ratio of symmetrical to antisymmetrical molecules. The type of curve obtained for each state as well as that of the averaged experimental data is shown in Fig. 40. It was found by Dennison that best agreement could be obtained by taking a value ⅓ for ρ.

By the use of catalyzing agents, Bonhoeffer and Harteck[53] have shown that at low temperatures this ratio may be greatly altered so that the para form predominates; but under the conditions of ordinary specific heat measurements the usual ratio ⅓ exists.

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[51] T. Hori, *Zeit. Phys.* **44**, 834 (1927).

[52] D. M. Dennison, *Proc. Roy. Soc.*, **115A**, 483 (1927).

[53] K. F. Bonhoeffer and P. Harteck, *Zeit. phys. Chem.*, 4 Abt. 1–2, 113 (1929.)

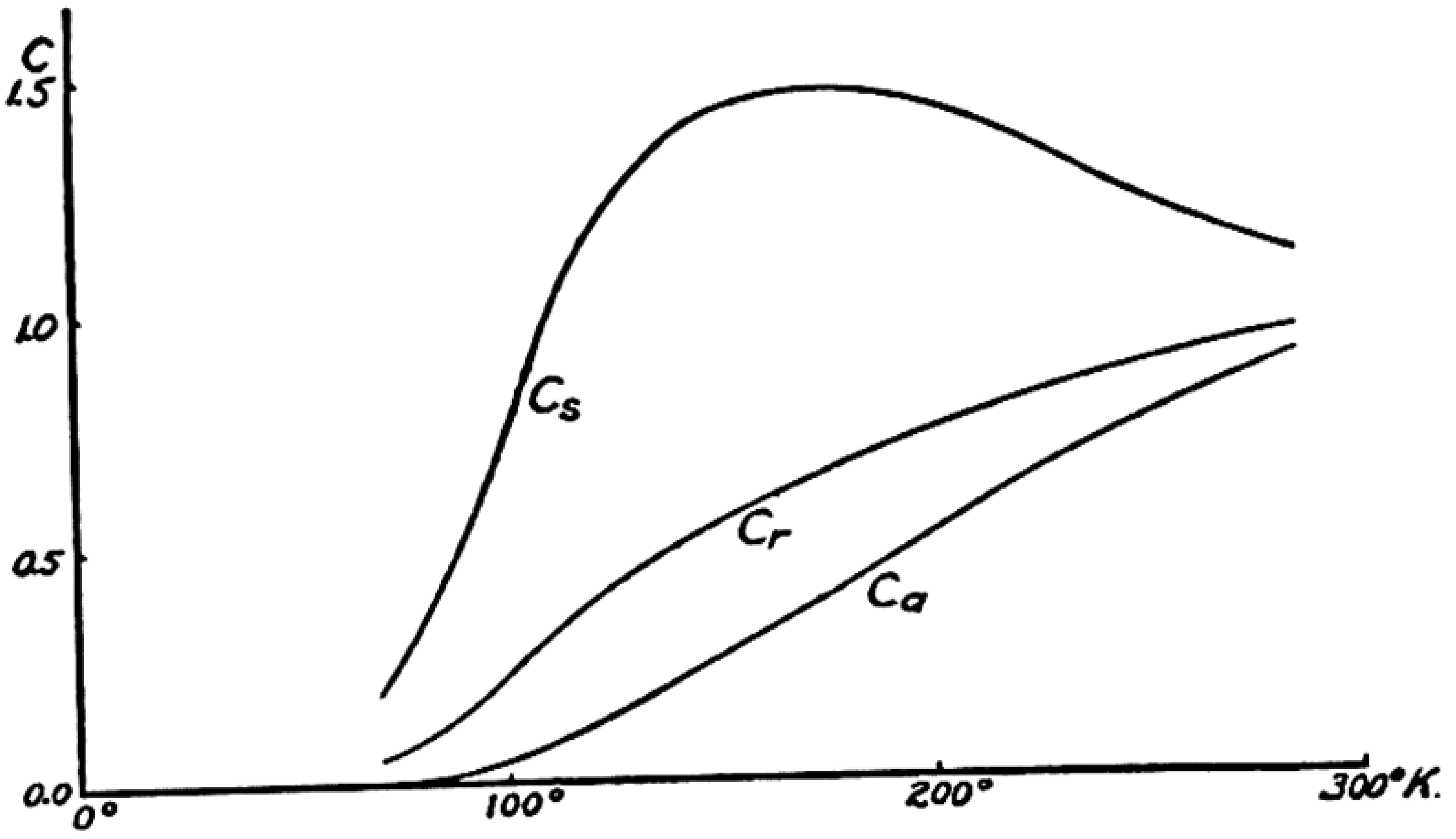

FIG. 40. The calculated variation with temperature in rotational specific heats for *para* hydrogen C_s and *ortho* hydrogen C_a.

PROBLEMS

1. If the bore of the stem of a Bunsen ice calorimeter is 0.2 sq. mm. in area, what is the sensitivity of the apparatus in calories per millimeter?

2. If in the electrical method of determining specific heat a current of 1.5 amperes, at an emf. of 20 volts, raised the temperature of 200 gm. of a substance 30° C. in 2 min., what is the specific heat of the substance?

3. In measuring the ratio of the specific heats of a gas (γ) by observing the velocity of sound using a Kundt tube, the vibrator has a frequency of 983 vibrations per second. Using air at 20° C. what would be the distance between positions of maximum loudness (half wavelength)? The temperature is now raised to 100° C. What change would be expected in the velocity and in γ?

4. In the Clément and Désormes method, gas is admitted into a container until a turpentine manometer indicates a pressure of 12 cm. in excess of atmospheric pressure. After tapping the valve and waiting for the system to come to equilibrium the manometer indicates a pressure in excess of atmospheric of 3.5 cm. What is the value of C_p/C_v? Explain the processes.

5. The clearance volume in a certain Diesel engine cylinder is one-sixteenth the maximum volume. If filled with a gas for which C_p/C_v is 1.4 at a pressure of 15 lb. per sq. in. and a temperature of 50° C. at the maximum volume, what temperature and pressure would be attained at the minimum volume assuming the compression to be a purely adiabatic process?

6. If C_p for iron is 6.4 calories per gram-mole, what is the value of C_v? Use both equation 56 and equation 57.

7. For air, $C_p = 0.237 \dfrac{\text{calories}}{\text{gm. deg. C.}}$; calculate C_v. Find R for air where the density $\rho = 0.00129$ gm. per cm.^{3} under standard conditions.

8. Show that for monatomic gases the velocity of sound is 0.745 times the average molecular velocity.

9. Using the data of page 271 calculate the velocity for each of the following in equilibrium at 100° C.: hydrogen molecule, oxygen molecule, and a free electron.

10. The coefficient of viscosity of oxygen at 25° C. is given as 200×10^{-6} poise (dyne sec./cm.^{2}). By using equation 16 and the result of problem 9, calculate the effective radius of the oxygen molecule.

11. Calculate by the Einstein equation the characteristic frequency of the atoms in the nickel lattice. Take C_p as 0.086 calories per gm. per deg. C. at −87° C. Use a substitution method, assuming two different frequencies ν and calculating the corresponding values of C_v. Then interpolate for the correct value.

CHAPTER III

THERMAL EXPANSION

Definitions. The linear dimensions of a body, like all its other physical properties, are found to vary as the temperature of the body is changed. With a slight change in temperature ΔT, a line of length L in the body will suffer a slight change in length ΔL. Experiment reveals the fact that the quantity ΔL is proportional both to ΔT and to the original length L. The magnitude of ΔL is also dependent upon some property of the material m of which the body is made. Hence, to summarize, ΔL varies as $mL\Delta T$. The units for measuring this property of the material m might well be chosen so that the proportionality is replaced by an equality sign. When so expressed, this property of the material is called the thermal coefficient of linear expansion and is usually represented by the symbol α.

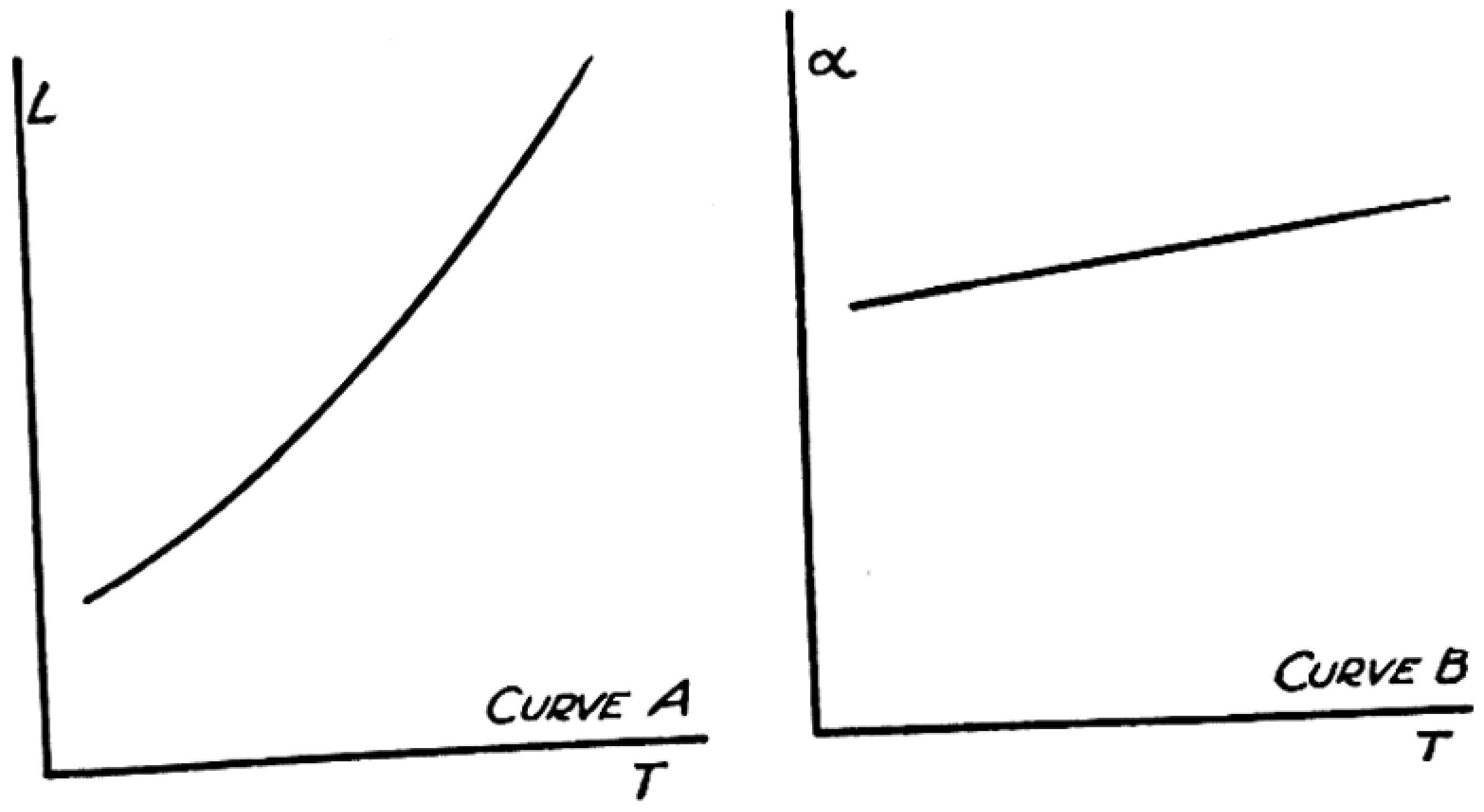

FIG. 41. Curves illustrating the variation in length and the change in coefficient of linear expansion of metals with temperature.

Hence it follows that

$$\alpha = \frac{1}{L} \cdot \frac{dL}{dT} \tag{1}$$

The quantity dL/dT is the slope of a length-temperature curve as shown in curve A, Fig. 41 (at some particular point), and L represents the total length in the material at the temperature at which the slope is taken.

For a given material the coefficient of linear expansion α is found to vary with the temperature. This variation as observed for a brass specimen is illustrated qualitatively in Curve B, Fig. 41.

It is sometimes desirable to obtain an average value for the thermal coefficient of linear expansion over a certain range in temperature. Such a quantity α_{average} is usually defined as follows:

$$\alpha_{\text{average}} = \frac{L_2 - L_1}{L_1(T_2 - T_1)} \tag{2}$$

In this expression, L_2 and L_1 are the lengths at the respective temperatures T_2 and T_1.

As the temperature of a body is changed, so also are its volume and the area of any surface drawn in the body. The thermal coefficient of volumetric expansion and the coefficient of superficial expansion (pertaining to area) are represented by the symbols β and δ respectively and are defined by the following equations:

$$\beta = \frac{1}{V} \cdot \frac{dV}{dT}, \quad \delta = \frac{1}{A} \cdot \frac{dA}{dT} \tag{3}$$

The quantities dV/dT and dA/dT are the slopes of the corresponding volume-temperature and area-temperature curves, and V and A are the particular values of the volume and area at the points at which the slopes are taken.

Isotropic and Anisotropic Substances. In isotropic substances the coefficient of linear expansion is independent of the direction in the substance at which it is observed. This class of substances consists of all amorphous solids, certain extended crystalline structures belonging to a regular class, for example, KCl, and all finely grained crystalline substances in which the minute granules have no preferred orientation. In anisotropic crystalline materials the value of α is found to vary as the line along which it is observed takes different orientations with respect to the crystal axes. In general, it is possible to choose three mutually perpendicular axes in a crystal (not necessarily the crystallographic axes) such that by assigning to each a coefficient of linear expansion, as α_1, α_2, and α_3, the dilation of the crystal as a whole with any change in temperature may be expressed. Such axes are called the principal axes of dilation. It may even happen for a particular substance that α_1 is positive and α_2 and α_3 negative. Such results were reported by Pfaff[1] for beryl and calcite. There exists then the possibility of choosing a direction in the crystal such that a rod cut along it will suffer no change in length as the temperature is changed.

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[1] F. Pfaff, *Pogg. Ann.*, **104**, 171 (1858); **107**, 148 (1859).

Equations Relating Length and Temperature. If in equation 2 the beginning temperature be taken as 0° C., then the length L_T at any temperature T° C. is related to the length L_0 at 0° C. as follows:

$$L_T = L_0(1 + \alpha_{\text{average}}\, T) \tag{4}$$

where α_{average} is the average value of the coefficient of linear expansion between 0° and T°. If this average value between 0° C. and any higher temperature T° C. is constant, then the true value of α must decrease at higher temperatures, since $\frac{dL}{dT}$ is constant and $\frac{1}{L}$ would decrease.

A constant value of α results in a relationship between length and temperature such that

$$L_T = L_0 e^{\alpha T} \tag{5}$$

This equation, in which L_T and L_0 are the lengths at T° C. and 0° C. respectively and e is the base of the Naperian system of logarithms, may be shown to follow from equation 1 by integration.

In general it is not possible to represent the behavior of solids so simply. On this account it is common practice to relate the length of a line in a solid body, to the temperature of the body empirically as follows:

$$L_T = L_0(1 + aT + bT^2 + cT^3 + \cdots) \tag{6}$$

where a, b, c, etc., are constants. For the common metals only the first two constants need be considered, and to a first approximation a and α_{average} are identical. Thus for copper[2] between −100° C. and 400° C.

$$a = 16.2 \times 10^{-6}, \quad b = 4.5 \times 10^{-9}, \quad c = -20 \times 10^{-12},$$
$$\text{and} \quad d = 23 \times 10^{-15}$$

The values of α for a few common substances are shown collectively in Table 5. These results have been obtained by various observers and show considerable divergence among themselves. The data recorded are the limiting values of the coefficient of linear expansion and the range in temperature over which the observations were made. In industrial applications it is apparent that for particular uses, materials with very low coefficients of expansion are desired. For other uses it may be equally important to have a material with a large coefficient. To obtain a relatively large displacement with a small change

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[2] H. Fizeau, *Compt. rend.*, **68**, 1125 (1869); F. Henning, *Ann. Physik.* **22**, 631 (1907); P. Hidnert, *Bur. Stan. Sci. Paper* 410, 1922.

TABLE 5

COEFFICIENTS OF LINEAR EXPANSION (α) FOR METALLIC ELEMENTS

Substance		Temperature Limits		Limiting Values $\alpha \times 10^6$ deg. C.$^{-1}$	
Name	Symbol				
Silver	Ag	−200 to	900° C.	16.1 to	20.5
Aluminum	Al	−200	600	18.2	28.7
Arsenic	As	10	90	3.86	
Gold	Au	−100	500	13.8	15.9
Bismuth	Bi	−183	270	12.2	15.7
Graphite	C	−163	1500	7.2	0.6
Calcium	Ca	0	21	25.0	
Copper	Cu	−250	−193	3.9	
		−187	1000	12.3	20.0
Iron	Fe	−190	900	9.1	16.5
Gallium	Ga	0	30	18.3	
Indium	In	10	90	24.8	
Iridium	Ir	150	1500	5.7	10.6
Potassium	K	0	58	70.5	83.3
Lithium	Li	0	178	51.2	
Magnesium	Mg	−150	500	23.4	29.6
Molybdenum	Mo	−190	750	5.1	6.4
Sodium	Na	0	50	72	
Nickel	Ni	−200	1000	11.6	19.0
Osmium	Os	10	90	5.70	
Lead	Pb	−200	300	19.5	32
Palladium	Pd	−200	1000	9.7	11.9
Platinum	Pt	−150	1000	7.9	11.5
Rubidium	Rb	0	38	90	
Rhodium	Rh	−180	100	6.5	8.6
Ruthenium	Ru	10	90	8.51	
Antimony	Sb	−190	100	10.2	11.8
Silicon	Si	−190	100	2.5	6.9
Tin, white	Sn	−163	230	16	24
gray	Sn	−163	18	5.3	
Tantalum	Ta	−78	400	5.9	6.5
Thallium	Tl	10	295	25.6	33.0
Tungsten	W	−190	2200	3.8	7.3
Zinc	Zn	−170	300	29.5	39.5

in temperature, bimetallic strips, composed of metals with widely different coefficients of expansion, may be utilized. Such a pair of metals in common use are brass and invar for which the difference in coefficients of linear expansion amounts to about 18×10^{-6} deg. C.$^{-1}$.

Relation between Linear, Surface, and Volumetric Coefficients. In isotropic solids an increase in temperature is accompanied by the same relative increase in the length of every line in the body. Hence all areas and volumes associated with the body must enlarge accordingly. If, for simplicity, the body be assumed cubic in form, then the volume V_T at the temperature $T°$ C. may be expressed in terms of the volume V_0 at 0° C., as follows, where L_T and L_0 are the lengths of the edge at the corresponding temperatures:

$$\begin{aligned} V_T &= V_0(1 + \beta T + \cdot\cdot\cdot) = L_T^3 = L_0^3(1 + \alpha T + \cdot\cdot\cdot)^3 \\ &= V_0(1 + 3\alpha T + \cdot\cdot\cdot) \end{aligned} \tag{7}$$

Since only first-order terms are carried along, β is the average thermal coefficient of volumetric expansion and is approximately equal to three times the average coefficient of linear expansion α_{average}. In a similar way δ, the average coefficient of superficial expansion may be shown to be equal to twice α_{average}.

Hysteresis Effects in Solids. Many solid substances, when heated and subsequently cooled, do not regain completely their original dimensions. Upon being heated a second time an elongation may result which is somewhat different from that observed during the first heating. Such hysteresis effects are to be expected in polycrystalline materials. These substances consist of an aggregate of minute crystalline grains varying somewhat in size, packed together in a purely random manner. In the first heating the size and the arrangement of the crystalline grains may be considerably altered. The observed change in volume of the body is the combined result of the dilation of the individual grains together with any alteration in their packing. This alteration in packing is not a reversible process with change in temperature.

Many metallic alloys show a remarkable growth of this nature over long periods of time. Invar, an alloy of 36.1% nickel and 63.9% iron, has an exceedingly small thermal coefficient of linear expansion[3] and on this account has been widely used in making secondary standards of length. However, this alloy is found to be subject to a continued growth with time and is therefore unsatisfactory for this purpose when a precise length is to be maintained for a long period.

A method of determining the coefficient of linear expansion of a substance by means of x rays will be described later. It will be seen that the results obtained by this method are free from any effects due to a rearrangement of the crystalline granules.

Variation of the Coefficient of Linear Expansion with Temperature. *The Grüneisen Rule:* The thermal coefficient of linear expansion of most pure metals is found to increase as the temperature of the specimen is raised.

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[3] Sieglerschmidt, *Mitteilungen Kaiser-Wilhelm Inst. Berlin*, **38**, 182, 1920. In equation 6 for temperatures from −200° C. to −20° C., Sieglerschmidt found for invar, $a = 0.25 \times 10^{-6}$, $b = -4.97 \times 10^{-9}$, and $c = -6.13 \times 10^{-12}$.

Grüneisen[4] investigated this property for many metals down to −170° C. By comparing the coefficient of linear expansion of a substance with its specific heat over the same range in temperature an interesting relationship was revealed. This may be summarized by saying that the ratio of the coefficient of linear expansion of a substance to its specific heat under constant pressure at the same temperature is constant at all temperatures. The data illustrating the constancy of this ratio for a few metals are shown collectively in Table 6. In the second column is the temperature at which the observation on the coefficient of linear expansion is made. These values of the coefficient of linear expansion, and the corresponding values of the specific heat C_p, are shown respectively in columns three and four. The quotients of the two quantities are shown in column five.

There is a slight increase in the quotient with increasing temperature for most metals. Iron between 500° C. and 800° C. and nickel at 300° C. give divergent values for the ratio. At these temperatures, transitions in the crystalline structure of these substances are known to occur. Metals in the liquid state do not conform to the rule. This relationship is of considerable importance since at the present time theories have been proposed which adequately explain the observed variation of the specific heat with temperature. It might be implied that a similar development is possible for the coefficient of linear expansion. It will be seen that according to the "third law of thermodynamics" (Nernst's heat theorem) both the specific heat and the coefficient of linear expansion of every substance should vanish at the absolute zero of temperature.

Variation of the Coefficient of Linear Expansion with Atomic Number. It is well known that if the atomic volumes (i.e., cubic centimeters per gram-atom) of the condensed elements be plotted with their atomic numbers, a curve with a remarkable periodicity results. At the peaks of the curve are the alkaline metals, lithium, sodium, potassium, cesium, etc. These are the elements which have a single valence electron in their outermost shell. At the minimum points on the curve are those elements having a four-electron configuration in the outer shell, such as carbon, silicon, and titanium. If a curve is drawn relating the coefficient of linear expansion and the atomic number an almost identical periodicity is revealed. This relationship is shown in Fig. 42.

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[4] E. Grüneisen, *Ann. Physik*, **26**, 211 (1908).

TABLE 6

The Coefficient of Linear Expansion and the Specific Heat under Constant Pressure for Certain Metals at Various Temperatures

Metal	Temperature	$\alpha \times 10^6$	C_p	$\frac{\alpha \times 10^6}{C_p}$
Aluminum	−173° C.	13.6° C.$^{-1}$	0.127 $\frac{\text{calories}}{\text{gm. °C.}}$	107
	−100	18.2	0.167	109
	0	23.0	0.210	110
	100	24.9	0.223	112
	300	29.0	0.243	119
	438	29.8	0.265	112
Iron	−87	9.0	0.086	105
	0	11.7	0.107	109
	100	12.7	0.116	109
	300	14.8	0.142	104
	500	17.0	0.190	89
	700	16.0	0.320	50
	900	24.5	0.218	112
Nickel	−87	10.1	0.086	117
	0	12.5	0.104	120
	100	14.0	0.116	121
	300	16.0	0.140	114
	500	16.8	0.133	126
Copper	−87	14.1	0.081	174
	0	16.1	0.091	177
	100	16.9	0.094	180
	400	19.3	0.108	179
	600	20.9	0.115	182
Palladium	−150	9.2	0.048	192
	−100	10.1	0.053	191
	0	11.5	0.058	198
	100	12.2	0.062	197
	875	15.5	0.076	204
Silver	−167	15.0	0.047	319
	−87	17.1	0.052	329
	0	18.3	0.056	327
	100	19.2	0.058	331
	500	23.1	0.066	350
	800	26.0	0.076	342

Forces Due to Expansion. If a beam is mounted in such a way that it is impossible for its length to change as its temperature is raised, then a state of strain will be developed in the beam. If the design of the beam is such that bending is not allowed, this strain will be a linear compression. The beam will be in the same condition that would have resulted had it been allowed to expand without resistance as the temperature was raised and then subjected to a compressing stress to restore the original dimension.

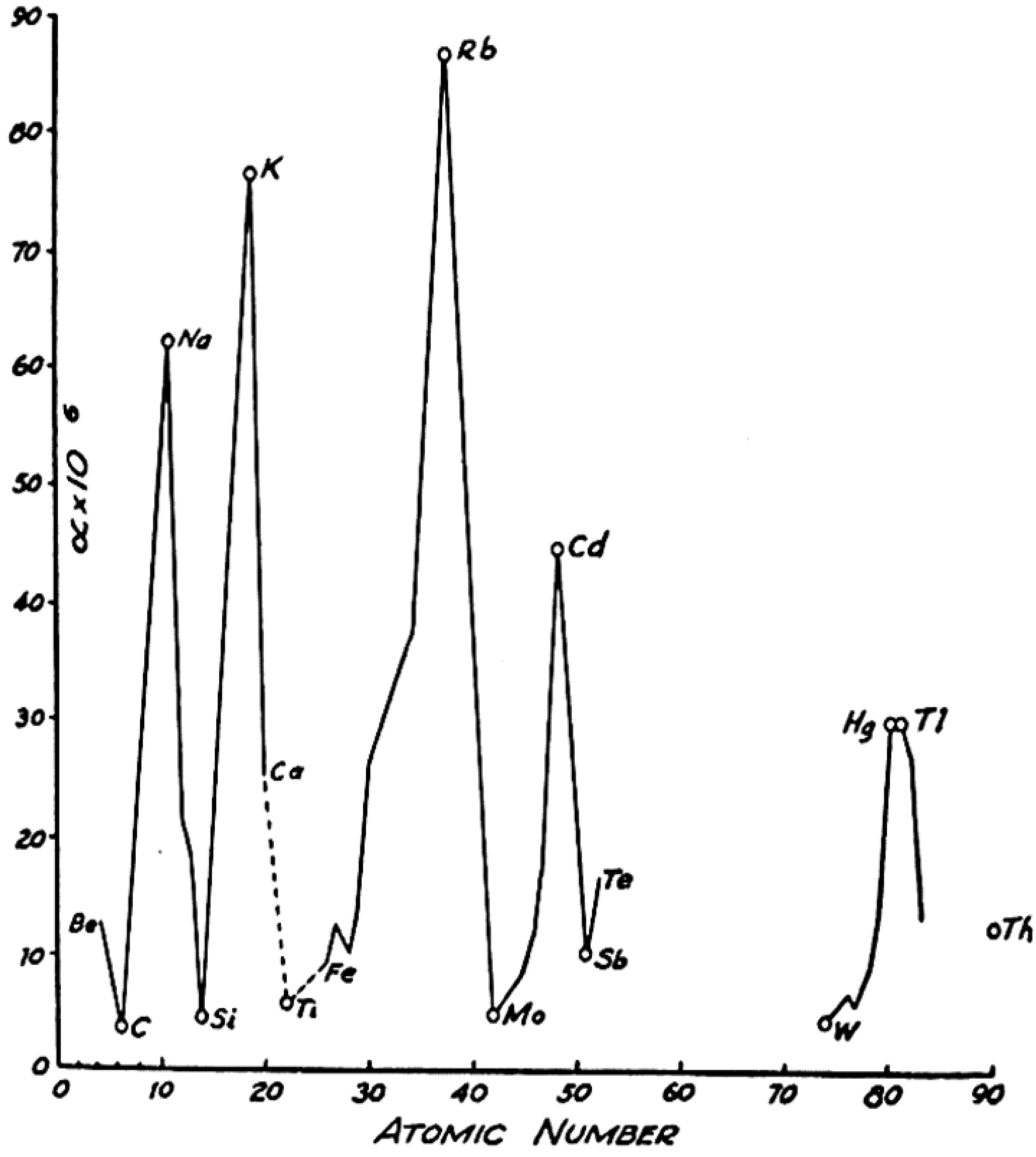

FIG. 42. The coefficient of linear expansion and atomic number for various elements.

From the definition of Young's modulus (Y.M.), the magnitude of the force F so developed for a linear strain $\Delta L/L$ may be directly expressed. Thus

$$F = (\text{Y.M.})\frac{\Delta L}{L} \cdot A = (\text{Y.M.})A \cdot \alpha \cdot \Delta T \tag{8}$$

where A denotes the sectional area of the expanding body, α is the coefficient of linear expansion, and ΔT is the change in temperature. It is apparent that the force exerted by the body tending to enlarge is entirely independent of the original length L. Thus bodies may be fractured even though made of homogeneous material if they are subjected to temperature gradients that are too steep. Similarly, fracture may occur in a body that is heated uniformly if it is composed of parts having different coefficients of linear expansion. Metals can be successfully sealed in glass if their expansion coefficients are not greatly different from that of glass. Fused quartz has a coefficient of linear expansion of only 0.54×10^{-6} deg. C.$^{-1}$. Consequently it can safely withstand almost any abrupt change in temperature.

EXPERIMENTAL METHODS FOR DETERMINING THE COEFFICIENT OF LINEAR EXPANSION

The experimental method to be employed in determining the coefficient of linear expansion of a specimen is dependent upon the form in which the material is available and the range in temperature over which it is to be investigated. The princlpal difficulty in most experimental procedures is the measurement of the small increment in length that results when the temperature of the specimen is changed by a small amount. Generally it is desirable to record a succession of such changes graphically so that the errors of individual readings will have little influence on the general form of the curve. Such data are shown plotted in Fig. 41, curve A. This smooth curve is drawn through the mean of the experimental points. The slope of the curve at any point divided by the length at that temperature gives the true coefficient of linear expansion at that temperature.

Historical. The need of an accurate knowledge of the change in length of a measuring rod as its temperature was varied appeared perhaps for the first time when it was attempted to make accurate surveys of land. Thus in the latter part of the eighteenth century Major General Roy had been entrusted to make an extended survey of Scotland. He first made a preliminary test[5] near London, using measuring rods made of glass and of brass, and observed the discrepancy between them. At his instigation a device was designed by Ramsden, an optician in London, to measure the change in length of a specimen when its temperature was changed by a definite amount.

In this method[6] the bar to be examined was placed in a horizontal position between two standard parallel bars of the same length. The two standard bars were maintained at a constant temperature by being immersed in baths of ice, while the temperature of the central bar could be varied. One of the standard bars was made to carry at each end a small lens. Similarly a lens was mounted at each end of the test bar so that the two lenses at each end made a rather long-focus microscope. These were adjusted so that they focused upon a cross wire carried at the ends of the second standard bar. One end of the specimen under test was fixed so that this microscope remained constantly in adjustment while at the other end the microscope was thrown out of adjustment as the temperature increased. A micrometer screw served to bring the object glass back to its original position and thus give the change in length that occurred in the expanding specimen.

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[5] W. Roy, *Roy. Soc. Phil. Trans.*, **35**, 22 (1785).

[6] For a more detailed description see Preston, *Theory of Heat*, Fourth Edition, p. 164.

In Paris, Lavoisier[7] and Laplace devised a method for magnifying many times the expansion of a specimen as its temperature was varied. In this method the bar being tested was arranged horizontally in a bath and fastened securely at one end. The other end was left free to move and pressed against a lever so that as the temperature of the bar was raised the lever was displaced, thereby rotating a horizontal telescope which was sighted upon a distant vertical scale. The magnification in length accomplished is thus equal to the ratio of the distance between the vertical scale and the axis of rotation of the telescope, and the distance between the axis of rotation of the telescope and the point of contact between the end of the bar and the lever pressing against it.

In the measurement of the French meridian degree, measuring bars were used whose variation in length with change in temperature had been determined. The method that was employed by Borda[8] consisted in comparing the expansions of two rods, one of which was taken as a standard. The two rods were firmly fastened together at one end. At the other end, adjacent scales were etched on the bars with graduations such that the scale on one of the bars served as a vernier moving over the scale on the second bar.

Under the auspices of an International Committee on Weights and Measures, a series of precise experiments was begun at Sèvres in 1878. The object of these investigations was an exhaustive study of the material to be used in making the prototypes of the international meter to be given to those countries which had signed in 1875 at the "Convention du Metre." The results of this work were reported from time to time in the *Travaux et mémoires du bureau international* and included the description of an elaborate device for determining the coefficient of linear expansion. A summary of the investigations was published by Benoit[9] in 1889. To determine the coefficient of linear expansion a comparative method was employed. Two microscopes were mounted upon a massive support which was maintained at a constant temperature. The microscopes were first focused upon lines etched upon the specimen being tested. The expansion of the specimen was found by means of a micrometer screw provided with each microscope. The specimen with its surrounding bath was mounted on a carriage so that it could be removed readily and a standard bar at a fixed temperature moved up to take its place. Materials investigated in this way were various types of glass, quartz, platinum, iridium, steel, brass, and many other metallic alloys.

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[7] A. L. Lavoisier died by guillotine in 1794. This investigation was first reported by J. B. Biot in 1816. See Biot, *Traité de physique*, Vol. 1, p. 146.

[8] See J. B. Biot, *Traité de physique*, Vol. 1, p. 164.

[9] J. R. Benoit, *Jour. Phys.*, **8**, 258 (1889).

Day and Sosman[10] in extending the range of the gas thermometer up to 1,553° C., i.e., the melting point of palladium, employed bulbs made of an alloy of platinum. It was in this case necessary to know precisely the coefficient of volumetric expansion of the material of which the bulbs were made. To do this, the coefficient of linear expansion of a bar made from the same material was determined. In this investigation the bar being tested was arranged in a horizontal position in a uniformly heated electric furnace. A finely graduated scale had been engraved on each end of the specimen, and these scales were observed by telescopes sighted through small windows in the top of the furnace. The two telescopes were mounted on a supporting base which was made of invar and kept at a uniform temperature.

The coefficient of linear expansion was found to be characteristic to some extent of the particular specimen of the material employed. Different test bars of the same material were found to give slightly varying results.

Numerous other precise determinations of coefficients of linear expansion have been reported. The experimental arrangements presented in the following paragraphs are representative of the methods that may be employed.

Vertical Quartz Furnace — Differential Method. A method in which is observed the difference in expansion between a specimen and an equivalent length of fused quartz was described by Henning[11] in 1907.

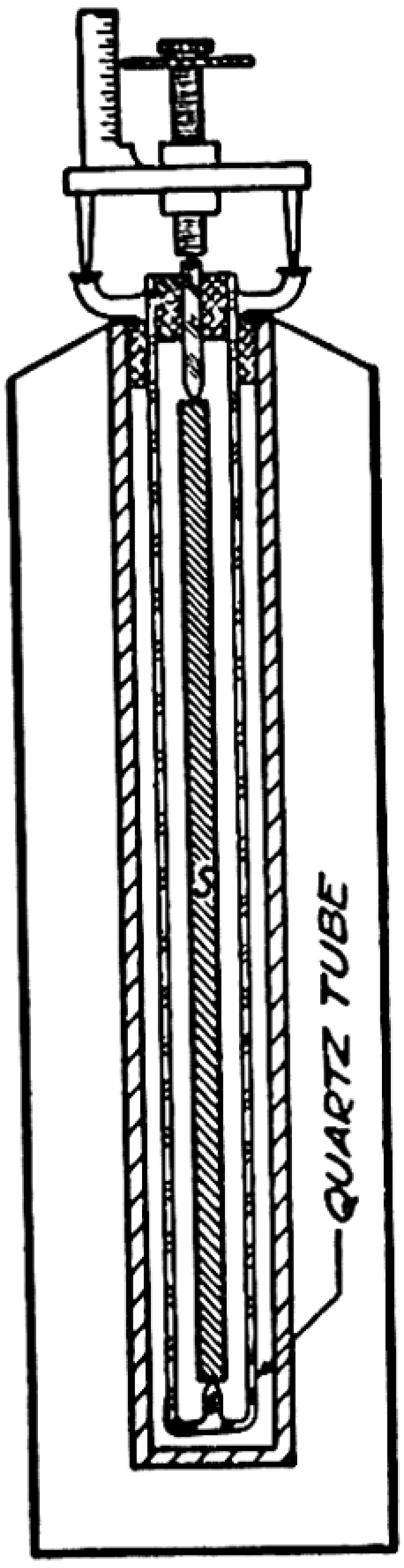

FIG. 43. Vertical quartz furnace for determining the coefficient of linear expansion.

This apparatus with slight modification as used by the author is illustrated in Fig. 43. This consists of a vertical, uniformly heated electric furnace in which is placed a cylindrical tube of fused quartz which is closed at one end. The specimen S under investigation is supported at the center of the tube on a specially arranged quartz stem fused at the bottom. At the top of the specimen there is supported a thin rod of quartz which communicates with the screw of a micrometer that is supported by the outer quartz tube. The length of the specimen being considerably shorter than that of the surrounding tube, variations in temperature at the ends are avoided. Temperatures may be measured conveniently by thermocouples. Assuming that, as the temperature of the furnace is altered, that of the outer tube and of the rod within change by the same amounts, then the expansion observed is the difference between the change in length of the rod S and an equivalent length of fused quartz. The apparent coefficient of linear expansion determined in this way may be converted to the true value for the specimen by the addition of the corresponding coefficient of linear expansion of fused quartz, which is small and well known.

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[10] A. L. Day and P. B. Sosman, *Am. Jour. Sci.*, **29**, 93 (1910).

[11] F. Henning, *Ann. Physik*, **22**, 631 (1907).

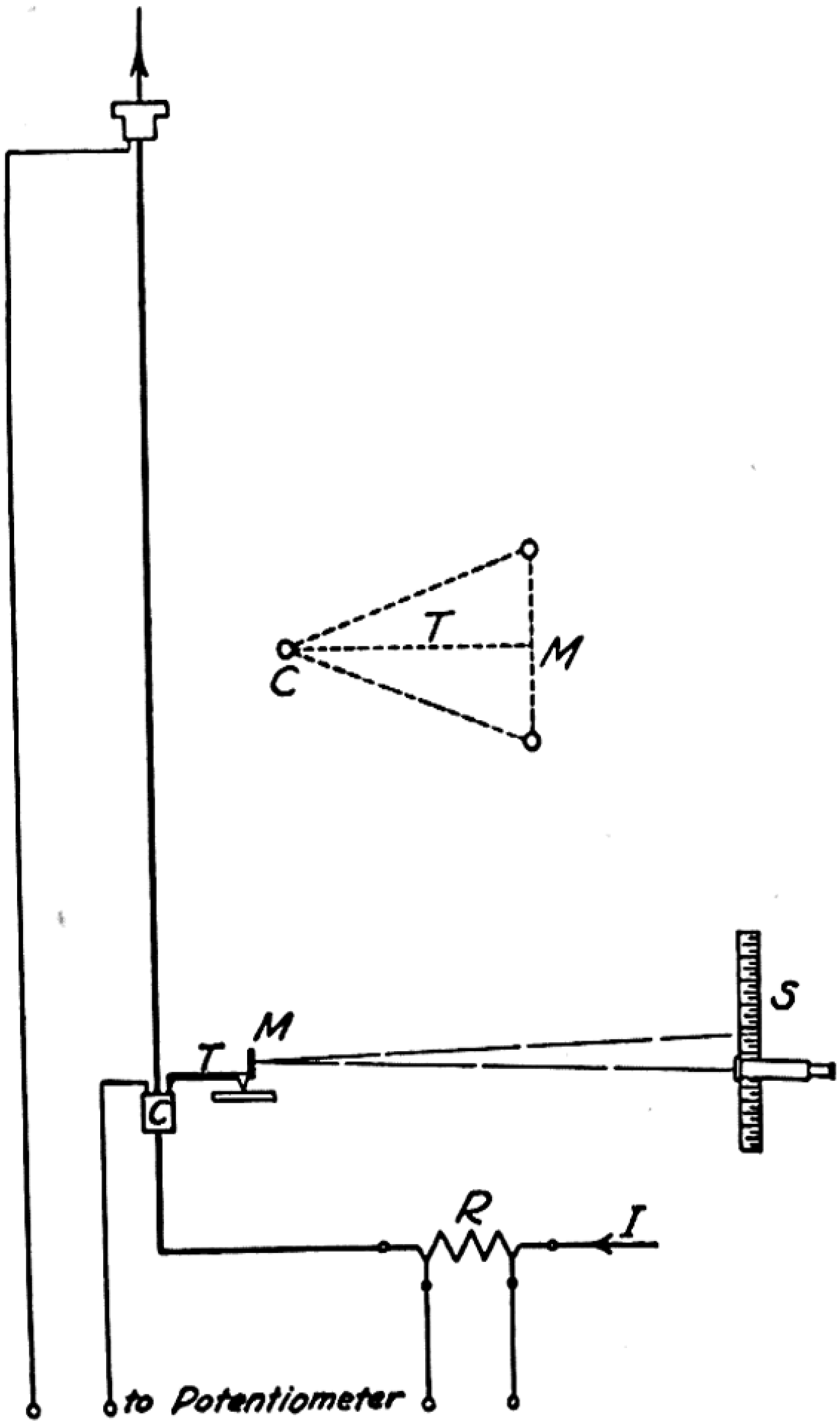

FIG. 44. Thermal expansion by the method of the optical lever.

Method of Optical Lever. An experimental arrangement in which the expansion of the specimen may be greatly magnified is illustrated in Fig. 44. The material under investigation in the form of a rod or wire is mounted vertically in a rigid support. At its lower end is a cylinder upon which rests the leg of a tripod T. The tripod carries a mirror M, and since the other two legs rest on the rigid support any vertical motion of the cylinder results in a rotation of M. This is arranged to reflect the image of a vertical scale to a telescope and thus magnify the extension of the specimen by the factor $2MS/T$, where MS is the distance between the scale and the axis of rotation of the mirror and T is the distance between the movable leg of the tripod and the axis of the mirror. The factor 2 is due to the relationship that if a mirror is rotated by a small angle θ then the reflected ray from a fixed source will suffer a rotation of 2θ.

The temperature of the specimen may be varied by passing through it any desired electric current. By connecting in series a standard shunt R and measuring the falls in potential across both it and the specimen, the resistance of the specimen is found. Any change in this resistance serves as an accurate indication of the change in temperature of the specimen. It may be observed that a non-uniform distribution of temperature along the length of the rod or wire does not lead necessarily to erroneous results, since for any element of length the change in length and the change in resistance are to a first approximation proportional. The temperature as measured in this way is an average or effective temperature for the entire length.

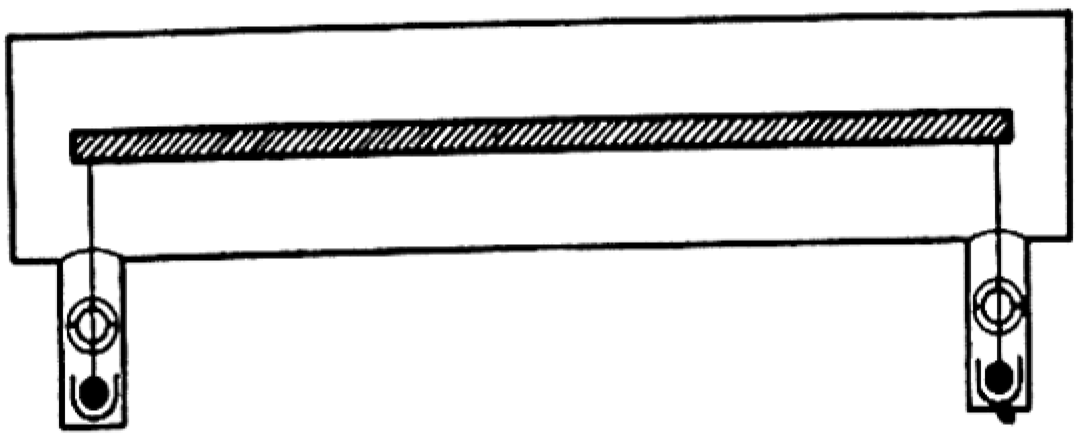

FIG. 45. Thermal expansion by the comparator method.

The Comparator Method as Used at the U. S. Bureau of Standards. When the specimen is available in the form of a relatively long bar then the expansion may be sufficient to be observed directly by a traveling microscope. After a careful survey of many classical experiments of this nature the following method has been employed at the U. S. Bureau of Standards to determine the coefficient of linear expansion. This method was used first[12] in the study of fused quartz and is shown in principle in Fig. 45. There is a remarkable similarity between the arrangement employed here and that described by Benoit as used at the International laboratory at Sèvres.

The specimen is mounted in a horizontal position in an electrically heated furnace. At each end, fine wires carrying weights are attached to the bar. These weights are submerged in oil, thereby keeping the wires vertical and quiet. A parallel invar base which is maintained at a constant temperature supports two microscopes which are focused upon the vertical wires. Simultaneous readings of the micrometer scale at each microscope yield the length of the specimen at any temperature. The furnace and specimen are mounted on a carriage so that they may be removed and a bar of standard length put in the place of the specimen. Many subsequent investigations[13] have been carried out in which the same method has been employed.

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[12] W. H. Souder and P. Hidnert, *Bur. Stand. Sci. Papers*, 524, **21**, 1 (1926).

[13] P. Hidnert, *Bur. Stand. Jour. Res.*, **2**, 887 (1929); **9**, 703 (1932).

Method of the Interferometer (Fizeau). A method of measuring the expansion of small crystalline specimens in terms of the wavelength of light was devised in 1860 by Fizeau.[14] This interferometer method is particularly applicable when only small-sized specimens are available and when the coefficient of linear expansion is very small. This method with modifications has been employed in many subsequent investigations.[15] The arrangement of the optical system as generally employed is shown in Fig. 46. Light from a mercury arc is directed by a small reflecting prism along the interferometer tube and is again reflected as a parallel beam into the furnace containing the specimen.

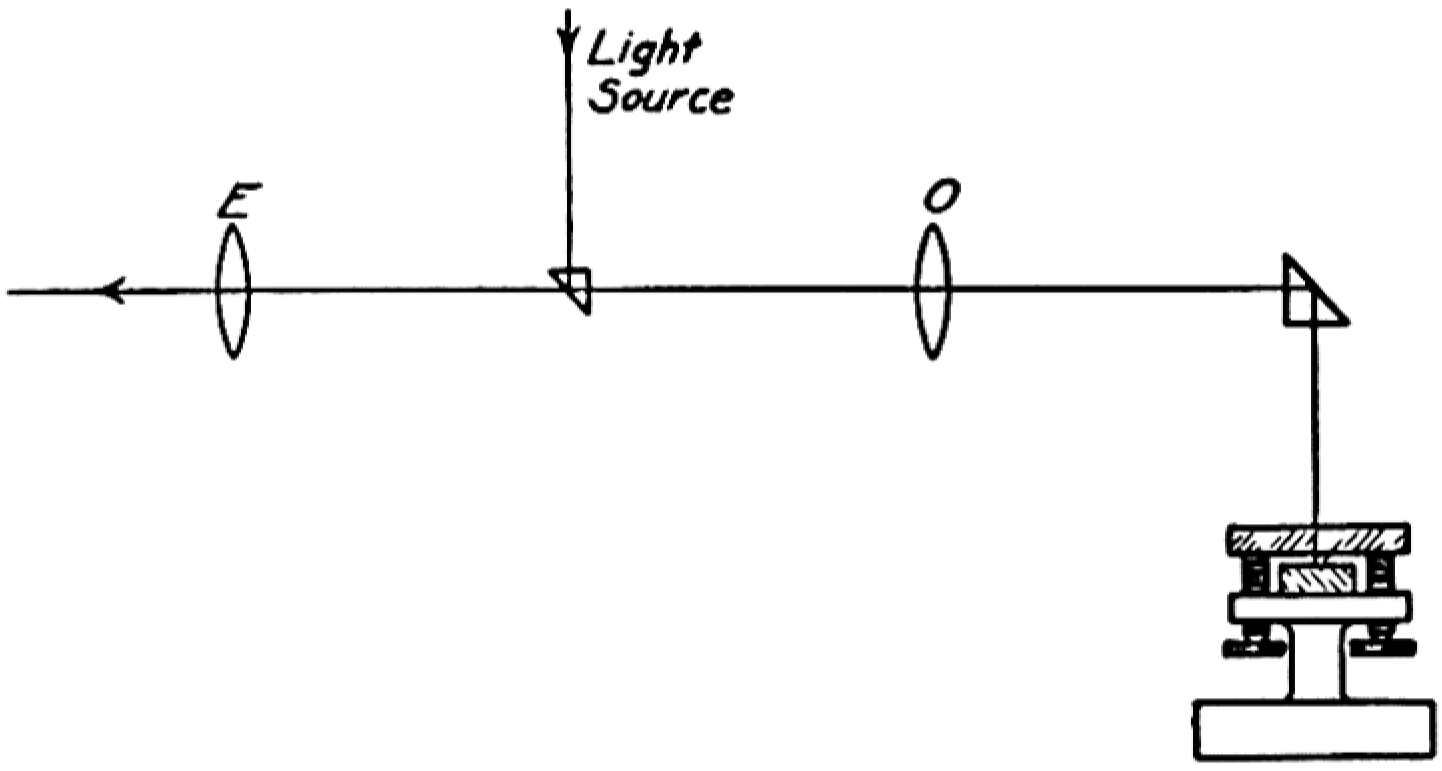

FIG. 46. Interferometer arrangement for determining the coefficient of linear expansion.

In Fig. 46 the material of the screws is the subject of the investigation. A quartz plate ground optically smooth is supported by the three screws. An auxiliary plate of quartz with an optically smooth top surface is placed on the table between the three screws. The position of the top plate is now adjusted until an interference pattern is observed due to the combination of light reflected from the bottom surface of the top plate and the top surface of the bottom plate. For monochromatic light this will appear as a series of bright and dark equally spaced parallel lines. The more nearly parallel the two surfaces, the greater is the distance between bright lines in the interference pattern.

As the temperature of the furnace is increased, the upper quartz plate is lifted by the expansion of the screws. At the same time the inner quartz plate grows thicker, thereby lifting its top surface. Any difference in these two expansions will cause the two optical surfaces to separate and thus cause a displacement of the fringe system as observed by a telescope at the end of the interferometer tube. A shift of one fringe means a separation of the two surfaces of one-half of one wavelength of the light employed. By counting the number of fringes that pass as the temperature is raised a definite amount, an apparent coefficient of linear expansion may be calculated. Thus

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[14] H. Fizeau, *Ann. chim. phys.*, **2**, 143 (1864).

[15] K. E. Abbé, *Wied. Ann*, **38**, 453 (1889); C. Pulfrich, *Zeit. Instrk.*, **13**, 365 (1893); H. M. Randall, *Phys. Rev.*, **30**, 216 (1910); W. F. Colby, *Phys. Rev.*, **30**, 506 (1910).

$$\alpha = \frac{1}{L} \cdot \frac{dL}{dT} = \frac{1}{L} \cdot \frac{\lambda}{2} \cdot \frac{dn}{dT} + \text{Correction} \tag{9}$$

where λ denotes the wavelength of the light used, L is approximately the thickness of the inner quartz plate, and dn/dT represents the number of fringes passing per degree change in temperature. As the index of refraction of the air changes with a change in temperature, the wavelength may be correspondingly corrected at each temperature.

The true coefficient of linear expansion of the specimen is found by adding to this apparent value the corresponding coefficient for quartz.

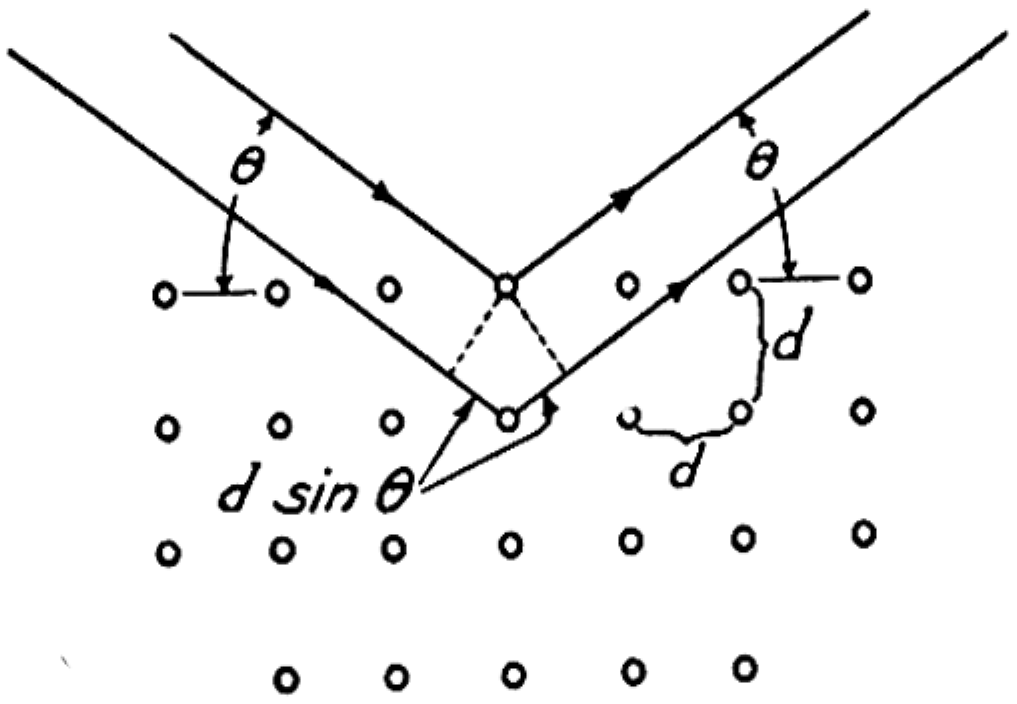

FIG. 47. The reflection of x rays by atomic layers in a crystal — Bragg law.

Coefficient of Linear Expansion by X Rays. (*A*) *Bragg Method.* If a monochromatic beam of x rays of wavelength λ is incident upon the natural cleavage face of a crystal, as shown in Fig. 47, reflection occurs at a certain particular angle (θ) satisfying the fundamental Bragg[16] law:

$$n\lambda = 2d \sin \theta \tag{10}$$

In this equation, d is the perpendicular distance between atomic planes parallel to the crystal face. The symbol θ represents both the angle between the incident x-ray beam and the atomic reflecting plane and the angle between the reflected x-ray beam and the same plane; n is a small integral number indicating the order of the reflection.

Now if an increase in temperature produces a real dilation of the crystal then the interplanar distance d in equation 10 becomes larger and consequently the angle θ at which a given wavelength will be reflected will be smaller (that is, $d \sin \theta$ is a constant). With modern spectroscopic apparatus these angles can be measured with a high degree of accuracy. To determine the coefficient of linear expansion along any particular direction in the crystal it is thus not necessary to know $n\lambda$ but only to be assured that it is constant. The interplanar distance (often called the grating constant or the lattice constant) d_T at the temperature $T°$ C. is $n\lambda/\sin\theta_T$ and at the temperature 0° C. it is $n\lambda/\sin\theta_0$. The coefficient of linear expansion is then

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[16] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, **88**, 428 (1912).

$$\alpha = \frac{d_T - d_0}{d_0 \cdot \Delta T} = \frac{\sin\theta_0 - \sin\theta_T}{\Delta T \cdot \sin\theta_T} \tag{11}$$

It is important to mount the crystal so that as it expands the effective plane of reflection remains always on the axis of the spectrometer.

By mounting the crystal on the axis of the spectrometer so that a different plane set is employed in reflection, the coefficient of linear expansion along any axis in an anisotropic crystal may be observed.

(*B*) *Hull*[17]*-Debye-Scherrer*[18] *Method.* Many materials are crystalline aggregates, that is, they are similar to the result that would be obtained if an extended single crystal were to be finely pulverized and then packed in a form having the desired shape. The minute crystalline granules ordinarily have a purely random distribution. Most common metals are of this polycrystalline nature. (An extended single crystal of copper will by a single bending transform to the ordinary polycrystalline form having greatly reduced ductility and electrical conductivity.)

If a fine pencil of monochromatic x rays is normally incident upon a thin sheet of a polycrystalline substance, then the probability exists that some of the little crystalline granules will be oriented just right to reflect x rays from every plane set that is characteristic of the crystal. Thus if a photographic plate is put back of the specimen a pattern consisting of concentric circles will be obtained. The innermost ring is due to those granules presenting the plane set having the largest lattice constant at the proper angle for reflection, since again $d\sin\theta$ is constant. Now if the temperature of the specimen is increased, the change in d will cause a corresponding reciprocal change in θ and hence in the diameter of the circle. Owing to the variation in the dimensions of photographic film with humidity it is essential that these patterns be taken on photographic plates. From the observation of two such patterns taken at different temperatures it is possible to observe simultaneously the expansions associated with each of the principal plane sets even in an anisotropic crystal. The coefficient of linear expansion of a metallic specimen observed by this method should be entirely independent of the history of the body, since the intergranular space can play no part in the x-ray reflection.

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[17] A. W. Hull, *Phys. Rev.*, **10**, 661 (1917).

[18] P. Debye and P. Scherrer, *Phys. Zeit.*, **18**, 291 (1917).

As an illustration of the application of the x-ray method, the results of Goetz and Hergenrother[19] upon a single crystal of bismuth may be noted. These observers made use of a Siegbahn x-ray spectrometer and measured the dilation in the lattice constant along a 111 axis as the temperature was altered in steps from −180° up to 265° C. Similar crystals have been studied by the usual macroscopic method[20] so that the results could be compared. At certain temperatures, notably at 75° C., by the usual method abrupt discontinuities had been observed in the coefficient of linear expansion. No such abrupt changes were observed by the x-ray method, showing that they must have been due to an alteration in the mosaic structure of the apparently single crystal. Moreover, the ratio between the coefficient of linear expansion and the specific heat noted by Grüneisen is somewhat variable at different temperatures when the usual values of α are used, whereas with the x-ray values the ratio was remarkably constant.

Expansion of Liquids. For fluids, only the coefficient of volumetric expansion has significance. The expansion of liquids is usually greater than that for solids. The determination of the coefficient of volume expansion of a liquid is generally complicated by the necessity of the liquid being in a container whose volume will also change as the temperature is changed.

Liquids whose coefficients of volumetric expansion are of particular interest are mercury and water. The former is of interest because of its extensive use in thermometers and barometers, and the latter because of its general utility value and its interesting behavior in having a maximum density at 4° C.

Method of Envelopes. The liquid to be investigated may be placed in a bulb-shaped container made of a material whose coefficient of volumetric expansion is known or may be found by a separate experiment. As the temperature of the whole is increased, the change in volume of the liquid is usually greater than that of the solid container. Consequently some liquid is either forced into a graduated stem provided with the bulb (dilatometer bottle) or it is allowed to overflow into a small dish where it is caught and weighed (weight thermometer).

The former arrangement is shown in Fig. 48. If subscripts zero and T denote initial and final conditions respectively, then the true volume of the liquid V_T at the temperature T is as follows:

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[19] A. Goetz and R. C. Hergenrother, *Phys. Rev.*, **40**, 643 (1932).

[20] J. K. Roberts, *Proc. Roy. Soc.*, **105 A**, 385 (1924).

$$\begin{aligned} V_T &= V_0(1 + \beta T) = V_a(1 + gT) = V_0(1 + aT)(1 + gT) \\ &= V_0[1 + (a + g)T + \cdots] \qquad (12) \end{aligned}$$

so that approximately

$$\beta = (a + g) \qquad (13)$$

In this equation, V_a is the apparent volume occupied by the liquid at the higher temperature T as indicated by the position of the meniscus on the stem; g is the coefficient of volumetric expansion of the material of the container; a is the apparent coefficient of volumetric expansion for the liquid, neglecting any change in volume of the container; and β is the true coefficient of volumetric expansion of the liquid.

The necessity of knowing the coefficient of volumetric expansion for the material of the container is a decided disadvantage in this method. Since it cannot be found from the container itself the coefficient of linear expansion of another specimen of the same material is usually found. It has been observed that this may have somewhat different properties from those of the specimen employed in the bulb.

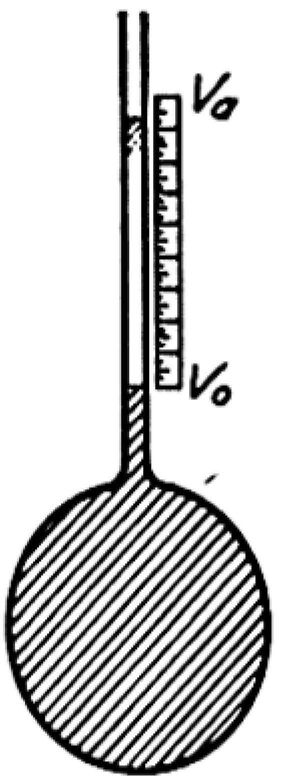

FIG. 48. The dilatometer.

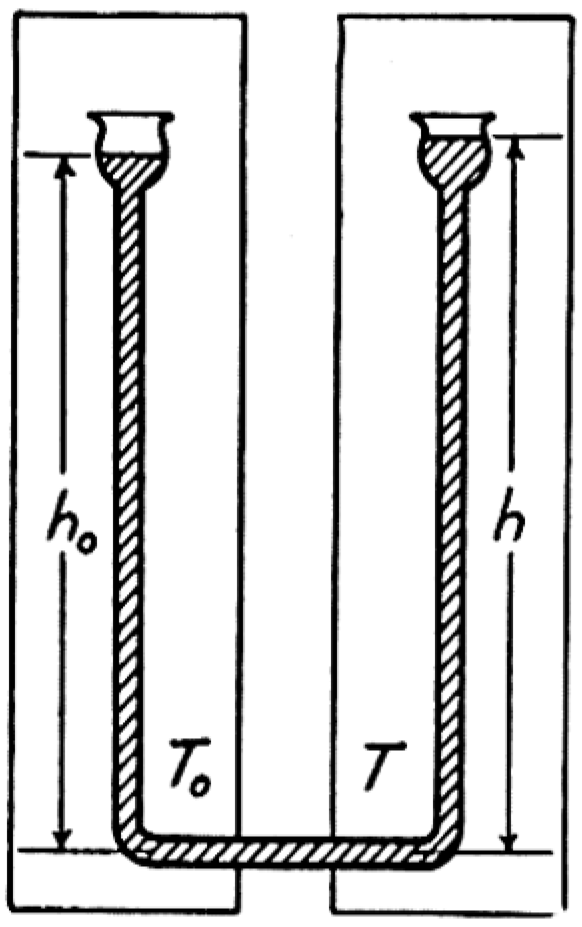

FIG. 49. Volumetric coefficient of expansion of liquids by balancing columns.

Method of Balancing Columns. In 1817, Dulong and Petit[21] described a method for determining the coefficient of volumetric expansion of a liquid, in which it was not necessary to know this same property for the material of the container. This apparatus in its simplest form is shown in Fig. 49. Two vertical tubes, communicating at the bottom through a horizontal capillary tube, are uniformly heated at two different temperatures. If one of the vertical tubes is maintained at 0° C. while the other is kept at some higher temperature $T°$ C., then the pressure P in the horizontal tube may be expressed in two ways. It may be considered as due to the head of liquid in either tube, so that

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[21] P. L. Dulong and A. T. Petit, *Ann. chim. phys.*, **7**, 127 (1818).

$$P = h_0 d_0 g = h_T d_T g \tag{14}$$

where d_T and d_0 are the densities of the fluid at the two temperatures T and 0° C., and h_T and h_0 represent the corresponding heights of the two columns of liquid measured up from the center of the horizontal capillary tube.

Since the mass of a substance is independent of its temperature, then for any definite amount of liquid

$$V_T d_T = V_0 d_0 = V_0(1 + \beta T) d_T \tag{15}$$

where β is the coefficient of volumetric expansion.

Hence

$$d_T = \frac{d_0}{1 + \beta T} \tag{16}$$

This value substituted in equation 14 gives for the average value of β between the temperatures $T°$ C. and 0° C.:

$$\beta = \frac{h_T - h_0}{T \cdot h_0} \tag{17}$$

The difference between the top levels in the two tubes $(h_T - h_0)$ may be observed by mounting the telescope of a vertical cathetometer so that it may be rotated readily from one tube to the other. The tubes are considerably enlarged at the top to avoid errors due to capillary attraction.

Various modifications of this apparatus have been employed by other investigators. Regnault[22] investigated the expansion of mercury using two different arrangements of vertical and horizontal tubes. The sensitivity of the apparatus is dependent upon the total length of the columns employed. In the experiments of Regnault the vertical tubes containing mercury were 1.5 meters long. The sensitivity was further greatly increased by Callendar and Moss,[23] who instead of using a single pair of hot and cold tubes, made use of six pairs of such tubes each of which was 2 meters long and connected in such a way that the observed difference in height was the cumulative effect for the whole system. The problem of insuring a uniform temperature throughout such a large volume as need be used here is not an easy one. In order to compensate for any uneven distribution of temperature, Callendar and Moss measured the temperature by a resistance thermometer the element of which was a winding of platinum distributed along the full length of the mercury tubes. Thus, even if the temperature were not uniform, the mercury tubes and thermometer element were both subject to the same average temperature.

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[22] H. V. Regnault, *Mém. Acad. Sci.*, **21**, 15–120 (1847).

[23] H. L. Callendar and H. Moss, *Phil. Trans.*, **211**, 1 (1911).

The results obtained in this experiment for mercury did not agree satisfactorily at low temperatures with those previously reported by Chappuis[24] using the method of the overflow thermometer. On this account the apparatus of Callendar and Moss with some alterations was duplicated at the international laboratory at Sèvres. In this case,[25] seven pairs of steel tubes each of which was 1 meter long comprised the vertical lengths. The horizontal connecting tubes were of larger diameter than had been used before. Values which were concordant with the best determinations by other methods,[26] were obtained.

For mercury the average value of the coefficient of volumetric expansion between 0° C. and any temperature $T°$ where T may take values from 0° up to 100° C. was found to be

$$\beta = 0.00018162884 + 8.5962282 \times 10^{-9}T \qquad (18)$$

This may be compared with the empirical expression of Callendar and Moss, who found that the average coefficient of volumetric expansion of mercury between 0° C. and any temperature $T°$ C. up to 308° C. was given by

$$\beta_T = 0.000180555 + 1.2444 \times 10^{-8}T + 2.539 \times 10^{-11}T^2 \qquad (19)$$

and for the fundamental interval 0° C. to 100° C.:

$$\beta = 0.0001820536$$

A consideration of the errors unavoidable in such experiments leads to the conclusion that the use of so many figures is not justified.

The Expansion of Water. The change in the density of water as its temperature is altered has been the subject of many investigations.[27] The anomaly in the behavior of the density between 0° C.

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[24] P. Chappuis, *Ann. poids mes.*, **13**, C3 (1907).

[25] P. Chappuis, *Trav. mém. bur. int.*, **17**, 7 (1917).

[26] F. J. Harlow, *Proc. Phys. Soc. London*, **24**, 30 (1911); **26**, 85 (1914); K. Scheel and W. Heuse, *Verh. deut. phys. Ges.*, **14**, 139 (1912).

[27] G. G. Hälström, *Ann. chim. phys.*, **28**, 56 (1825); C. Despretz, *ibid.*, **73**, 296 (1840).

and 4° C. was demonstrated in 1804 by Hope.[28] It was shown by Amagat[29] that the temperature at which the maximum density occurs is dependent upon the pressure. For each increase of one atmosphere in pressure the temperature of maximum density recedes from 4° C. toward zero by 0.025° C., so that under a pressure of 160 kg. per $cm.^2$ maximum density occurs at 0° C. Chappuis[30] determined the density of water at higher temperatures. He made use of a dilatometer bulb of platinum-iridium connected to a manometer containing mercury, so that as the water expanded a definite amount of mercury was expelled and weighed. The densities found for water from 0° C. to 100° C. were found to vary with temperature in such a way that the results could not be well represented even by an equation with four empirical constants.

Expansion of Gases. In the expansion of liquids and solids with change in temperature the influence of pressure is of secondary importance. With gases, however, this is not the case, because the volume is influenced sensibly by small changes in pressure. The coefficient of volumetric expansion thus has a definite value only when the pressure is qualified. For a constant pressure this quantity will be represented by the symbol β_V.

Equality of Coefficients for an Ideal Gas. Having agreed to measure temperature by the normal hydrogen thermometer, then the relationship between pressure and temperature for hydrogen is definitely established. Thus the pressure P_T at any temperature T° C. may be expressed in terms of the pressure P_0 at 0° C. as follows:

$$P_T = P_0(1 + \beta_P T) \tag{20}$$

where β_P is the zero coefficient of pressure for hydrogen and is by agreement a constant, that is,

$$\beta_P = \frac{1}{P_0} \cdot \frac{dP}{dT} \quad \text{and} \quad \frac{dP}{dT} \text{ is constant}$$

If the gas obeys Boyle's law, then it must follow for that gas that β_P and β_V are identical. This may be shown to follow by allowing the temperature of a certain amount of gas at 0° C. to change to a higher value T. First, consider the change to take place under the condition of constant pressure and then again let the same change in temperature take place under the condition of constant volume. From Boyle's law the product of the pressure and the volume of a given amount of gas at a temperature T is dependent solely on the temperature, so that

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[28] T. C. Hope, *Ann. chim.*, **53**, 272 (1805).

[29] E. H. Amagat, *Compt. rend.*, **116**, 946 (1893).

[30] P. Chappuis, *Ann. physik*, **63**, 202 (1897); *Ann. poids mes.*, **13**, C3 (1907).

$$(PV)_T = P_0V_T = P_TV_0 = P_0V_0(1 + \beta_V T)$$
$$= P_0V_0(1 + \beta_P T) \tag{21}$$

Hence
$$\beta_P = \beta_V \tag{22}$$

Thus temperatures measured by a constant-pressure gas thermometer should agree with those as measured by a constant-volume gas thermometer provided the gas obeys Boyle's law.

The true coefficient of pressure is not a constant for an ideal gas. For

$$\beta_P = \frac{1}{P}\cdot\frac{dP}{dT} \tag{23}$$

and although dP/dT is constant at all temperatures, P increases with temperature, and hence β_P (true) decreases with increasing temperature.

Method of the Gas Thermometer. The apparatus for determining the coefficients of expansion of a gas generally takes the form of a constant-volume or of a constant-pressure gas thermometer. One of the first investigations of this nature was that carried out by Regnault[31] using air, hydrogen, carbonic acid, and many other gases at pressures from one to four atmospheres. The apparatus as used in this experiment is shown in Fig. 50. The gas under investigation is placed in the bulb A at any desired pressure through the connecting tube cp. The pressure of the gas is measured by the open tube manometer $FHIJ$. The level of mercury in the tube FH is always adjusted to the position α by adding or withdrawing the necessary amount of mercury. The bulb A, whose volume is V_0 when placed in a bath at 0° C., contains gas under the pressure P_0. Then with the bulb at T° C. the pressure P is observed. The difference in these pressures, such as $\gamma - \beta$, is represented by ΔP. The volume v in the connecting tube $BCEF$ called the "dead space" is at some average temperature T' which does not alter appreciably when the temperature of A is changed. Equation 2, in Chapter I, for the total mass of the gas in the bulb and dead space before and after heating, when solved for the coefficient of expansion β gives

$$\beta = \frac{\Delta P\left[1 + \frac{v}{V_0} + \frac{P}{\Delta P}gT\right]}{P_0T\left[1 - \frac{P}{P_0}gT' - \frac{\Delta P}{P_0}\cdot\frac{v}{V_0}\right]} \tag{24}$$

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[31] H. V. Regnault, *Ann. chim. phys.*, 3 Series, **4**, 43 (1842).

where g is the coefficient of volumetric expansion of the material of which A is made. Care must be taken to avoid errors due to the pressure of water vapor. Careful determinations of the thermal coefficients of pressure for carbon dioxide, nitrogen, and hydrogen, using similar apparatus, have been made by Chappuis.[32] Using hydrogen at 0° C. under a pressure of 100 cm. of mercury, and observing the pressure at 100° C., Chappuis expressed the zero coefficient of pressure to be

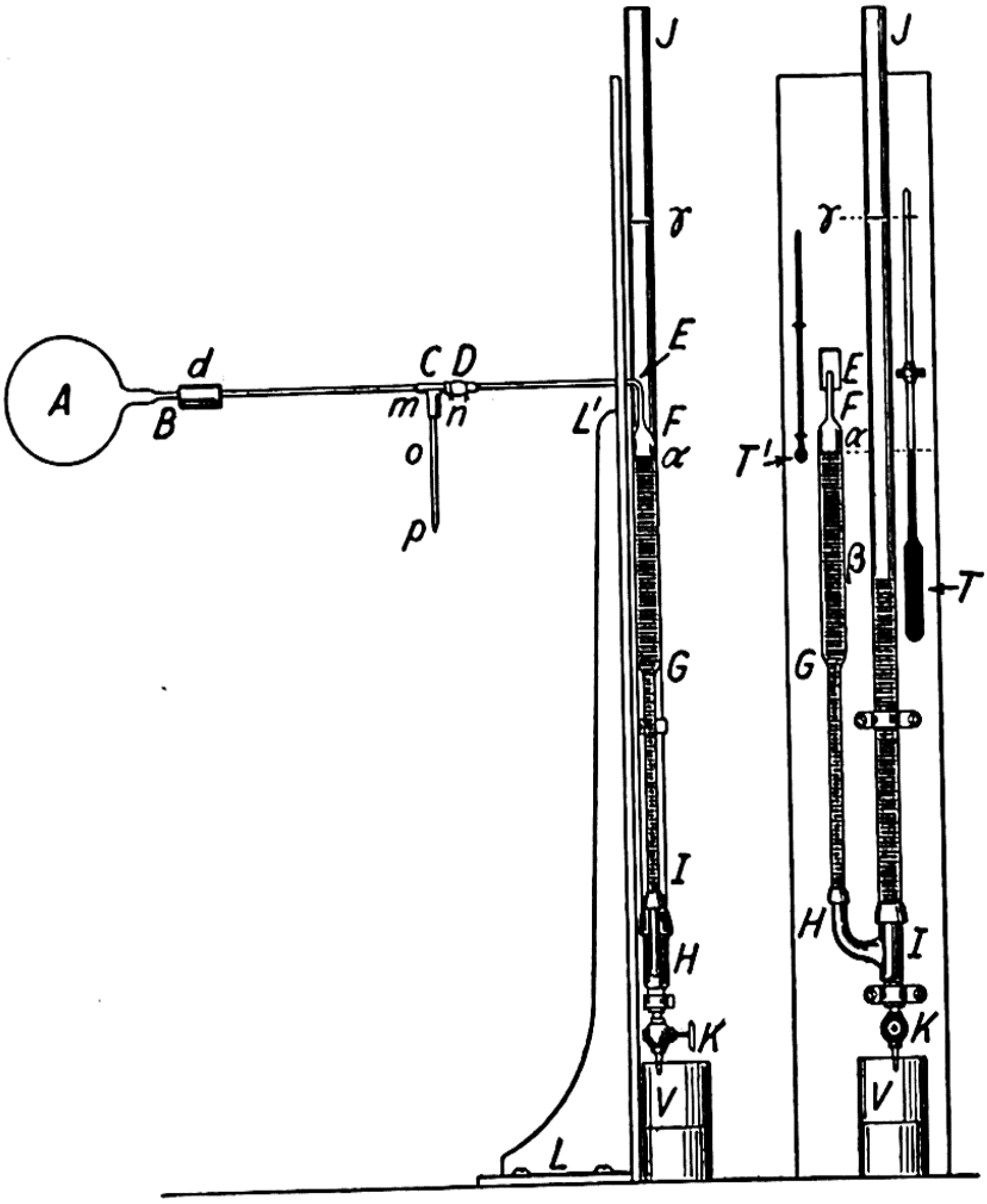

FIG. 50. The apparatus of Regnault for studying the expansion of gases.

$$\beta_P(\text{Hydrogen}) = 0.00366254$$

This indicates for the absolute zero a temperature of $-273.3°$ C.

All gases deviate from the ideal gas laws at higher pressures and conversely they approach an ideal state at zero pressure. Thus Henning and Heuse[33] measured both β_P and β_V for helium, hydrogen, and nitrogen at pressures up to 1,100 mm. of mercury. In each case they used the two fixed temperatures 0° and 100° C. These values were then plotted for all three of the gases and the straight lines drawn through each set of points were extrapolated to zero pressure. Although the data appear insufficient, lines were drawn to intersect at a common point as shown in Fig. 51. The coordinates of the intersection point were $P = 0$, $\beta = 0.00366041$. This corresponds to an absolute zero of −273.19° C.

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[32] P. Chappuis, *Trav. mém. bur. int.*, Vol. 6, 1888.

[33] F. Henning and W. Heuse, *Zeit. Phys.*, **5**, 285 (1921).

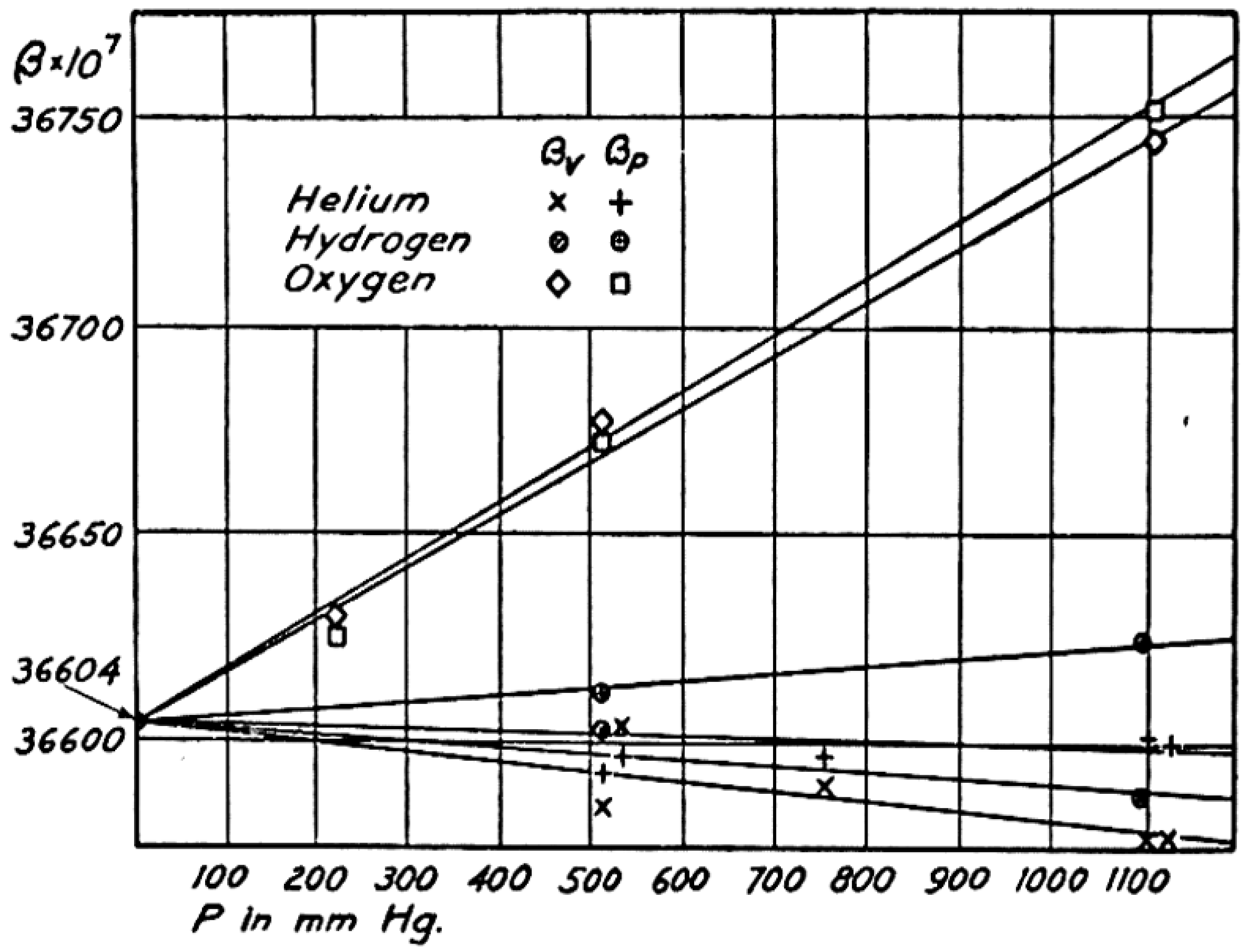

FIG. 51. Effect of pressure on the coefficients of expansion for helium, hydrogen, and oxygen (Henning and Heuse).

QUESTIONS AND PROBLEMS

1. If the true coefficient of linear expansion of a substance is a constant at all temperatures show that $L_T = L_0 e^{\alpha T}$ where L_T is the length at any centigrade temperature T.

2. Develop a relationship between the linear, superficial, and volumetric thermal coefficients of expansion for a substance.

3. A steel beam has a sectional area of 200 sq. cm. and is supported at each end so that it cannot expand. If its temperature is uniformly raised 40° C. what force is exerted upon the supports? Young's modulus for the steel is 20×10^{11} dynes per cm.^{2}.

4. In the interferometer method of determining the coefficient of linear expansion of a nickel specimen, a cylindrical ring of the material 1 cm. long is used to support the top quartz plate. Another quartz plate 0.92 cm. thick is placed within the nickel cylinder so that its top surface together with the under surface of the top plate gives rise to an interference fringe system. How many fringes will pass in the eyepiece when the temperature of the whole is raised 100° C., if a mercury arc is used as a source of light? ($\lambda = 0.0000546$ cm.) Assume α (quartz) $= 0.43 \times 10^{-6}$; α (nickel) $= 13.5 \times 10^{-6}$ (deg. C.)$^{-1}$.

5. An increase in pressure of 1 lb. per sq. in. decreases the volume of a block of steel by one part in twenty-eight million. How great a pressure would be produced by a 40° C. rise in temperature if the steel were kept from expanding?

6. If two flat metallic strips of dissimilar metals are riveted together and heated, show that the radius of curvature of the resultant arc is independent of the original length of the strips. Design such a bimetallic strip that when fastened securely at one end and heated 20° C. a lateral motion of the other end of approximately 1 mm. results. Sketch. What is the final radius of curvature?

7. A steel ($\alpha = 0.000011$ deg. C.$^{-1}$) tape is correct at 20° C. The distance between two stations is measured with this tape at 0° C. and found to be two miles. What is the true distance between the stations?

8. Discuss the possibility of determining linear coefficients of expansion by means of x rays.

9. An overflow bottle of crown glass ($\alpha = 8.9 \times 10^{-6}$ deg. C.$^{-1}$) weighs 6 gm. when empty and 200 gm. when filled with mercury at 25° C. What would be the expected weight at 100° C.?

CHAPTER IV

TRANSFER OF HEAT — CONDUCTION AND CONVECTION

Definitions. Experiment shows that the quantity of heat q transferred across a layer of material having parallel plane faces maintained at different temperatures T_2 and T_1, where T_2 is greater than T_1, is dependent upon the following factors: the difference in temperature $(T_2 - T_1)$, the area A, the time t, the thickness of the layer l, and some property of the material m. These factors enter in such a way that

$$q = cmAt\,\frac{T_2 - T_1}{l} \tag{1}$$

where c is a proportionality constant.

The property of the material m which, other things being equal, determines the quantity of heat transferred, might well be measured in units such that the proportionality factor c in the above equation is equal to unity. This quantity, which is usually represented by κ and is called the thermal conductivity of the material, is thus given by

$$\kappa = \frac{q}{Agt} \tag{2}$$

where g is the temperature gradient, that is, it is the fall in temperature per centimeter as represented by $(T_2 - T_1)/l$ or more exactly dT/dl.

In common practice, κ is expressed in calories per square centimeter per second for a temperature gradient of 1° C. per cm. The energy transferred per second q/t may also be expressed in joules per second or watts. The direction of flow of heat must be in the opposite sense to that of the temperature gradient since heat flows from higher to lower temperatures. This may be represented by introducing a negative sign before q in the above equation.

In English engineering practice, κ is often expressed in Btu. per hour per square foot with a normal temperature gradient of 1° F. This English unit is equivalent to 1.2404 cal. cm.^{-1} deg. C.^{-1} sec.^{-1}.

Flow of Heat, General Differential Equation. Fourier, in his *Théorie analytique de la chaleur* (1822), was perhaps the first to treat in a rigorous way the problem of the flow of heat. It is indeed of interest that the treatment of the thermal problem so ably dealt with by Fourier was many years later by a simple change in nomenclature able to fit analogous problems in electricity and magnetism.

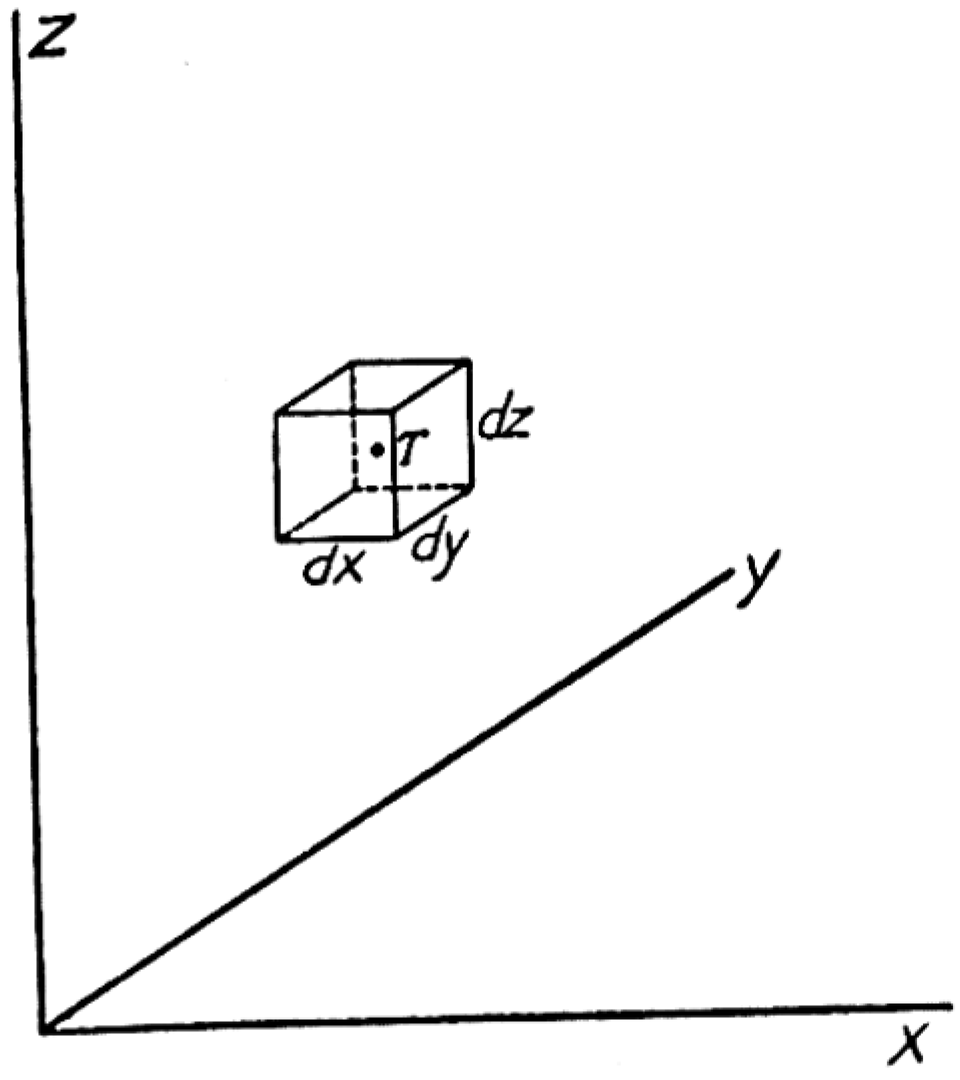

FIG. 52. Elementary cell in the three-dimensional flow of heat.

In the general case, the flow of heat may be regarded as the consequence of any uneven distribution of temperature whatever, in three-dimensional space. Let us imagine a small rectangular parallelopiped with edges *dx*, *dy*, and *dz* parallel to the mutually perpendicular *x*, *y*, and *z* axes as shown in Fig. 52. Imagine the elementary parallelopiped as having the temperature T at its center and being of such minute dimensions that the rate of variation of temperature along an edge may be considered to be uniform. Hence, if the temperatures be regarded as diminishing toward large values of x, then the rate of change of temperature with distance, represented by $\partial T/\partial x$, is negative. The temperature in the left ($dy\,dz$) face becomes $T - (\partial T/\partial x) \cdot dx/2$, and in the right face $T + (\partial T/\partial x) \cdot dx/2$.

There will then be a component of heat flow from left to right in the x direction whose inflow into the elementary parallelopiped is, per second,

$$\left(\frac{\text{Quantity in}}{\text{Second}}\right)_x = -\kappa A g = -\kappa dy\,dz \frac{\partial\left(T - \dfrac{\partial T}{\partial x}\cdot\dfrac{dx}{2}\right)}{\partial x} \tag{3}$$

κ is the thermal conductivity of the material and is assumed to be constant. In the same time the outflow through the opposite face is

$$\left(\frac{\text{Quantity out}}{\text{Second}}\right)_x = -\kappa dy\,dz \frac{\partial\left(T + \dfrac{\partial T}{\partial x}\cdot\dfrac{dx}{2}\right)}{\partial x} \tag{4}$$

Hence the net gain in heat per second in the volume element due to the x component of flow is the difference between (3) and (4) or

$$\left(\frac{\text{Net gain}}{\text{Second}}\right)_x = \kappa \cdot dy \cdot dz \cdot dx \cdot \frac{\partial^2 T}{\partial x^2} = \kappa \cdot dV \cdot \frac{\partial^2 T}{\partial x^2} \tag{5}$$

Considering in turn the y and z components of flow, similar expressions are obtained with $\partial^2T/\partial y^2$ and $\partial^2T/\partial z^2$, respectively, in place of $\partial^2T/\partial x^2$. Then for the three directions simultaneously the total net gain per second is

$$\kappa \cdot dV \cdot \left[\frac{\partial^2T}{\partial x^2} + \frac{\partial^2T}{\partial y^2} + \frac{\partial^2T}{\partial z^2}\right] = \kappa \cdot dV \cdot \nabla^2T \tag{6}$$

∇^2 is an abbreviation for the operator indicated within the bracket. Now if the inflow exceeds the outflow there must be an accompanying elevation in the temperature of the elementary volume per second $\partial T/\partial t$, so that

$$\kappa \cdot dV \cdot \nabla^2T = \rho dV \text{ (S.H.) } \frac{\partial T}{\partial t} \tag{7}$$

where ρ is the density of the material and (S.H.) represents its specific heat. Then:

$$\nabla^2T = \frac{\rho \text{ (S.H.)}}{\kappa} \cdot \frac{\partial T}{\partial t} = C\frac{\partial T}{\partial t} \tag{8}$$

The quantity C which is written for ρ (S.H.)/κ is thus a constant of the material. Kelvin gave to its reciprocal $1/C$ the name "diffusivity" of the substance. It will be seen that the diffusivity is an important factor in determining the velocity of a thermal disturbance through the medium.

One might hope to find from the solution of equation 8, for a given set of initial temperatures, either information regarding the variation in temperature at any point in space as time elapses, or at any particular instant what the distribution in temperature is throughout all space. Using any boundary conditions whatever, it usually is not possible to obtain satisfactory particular solutions of this equation. Only for a few relatively simple cases can it be dealt with so as to yield solutions that are of value.

Steady State — One Dimension. If heat be supplied in such a way that the temperature of every element of volume attains a value which is invariable with time, then everywhere $\partial T/\partial t = 0$. This condition is termed the "steady state." Now if boundary conditions be chosen such that the heat flow is in one direction only, taken, say, in the x direction, then equation 8 reduces for the steady state to

$$\frac{\partial^2T}{\partial x^2} = 0 \tag{9}$$

Successive integrations of this equation give

$$\frac{\partial T}{\partial x} = a \tag{10}$$

and

$$T = ax + b \tag{11}$$

where a and b are constants of integration.

A typical case of this kind is a homogeneous fire wall with the temperature maintained at some constant value T_m at one side where $x = 0$. At the other side, where $x = l$, let $T = T_0$. Then the temperature T_x at any intermediate point x is:

$$T_x = T_m - \frac{x}{l}(T_m - T_0) \tag{12}$$

Thus the temperature gradient is constant throughout the wall, and the temperature falls linearly with increasing distance normal to the equitemperature surface.

Experimental — Unidirectional Flow. A very simple and straightforward method may be employed to determine the thermal conductivity of a specimen when the material is available in the form of sheets. In its simplest form one must observe the quantity of heat transmitted per second by a layer of given dimensions when one surface is maintained at some constant temperature T_2 sufficiently long for the temperature of the other face to become steady at some value T_1. The heat may be supplied electrically, so that in the steady state the heat furnished per second is also that transmitted by the test specimen. The temperature difference $T_2 - T_1$ may be observed perhaps most easily by a differential thermocouple. Then for the steady state

$$\kappa = \frac{EIl}{JA(T_2 - T_1)} \tag{13}$$

In this expression EI is the electrical power in joules per second, J is the mechanical equivalent of heat, A denotes the common area of the heater and specimen, and l is the thickness of the specimen, or more exactly, the distance between the hot and cold junctions of the differential thermocouple. For relatively good conductors the thermojunctions should not be placed on the outer surface of the layer but should be imbedded in drill holes made in from the edge of the specimen. This is necessary, since in practice the fall in temperature across the surface film of metals might be many times the fall in temperature within the metal itself. In the case of thermal insulating materials this surface film is of relatively small importance.

To make sure that the power as measured is solely that transmitted by the specimen under test, various " guard ring " devices may be employed. Figure 53 shows a very satisfactory arrangement for tests of this nature. The heat is supplied electrically in a central heating plate, having symmetrically placed, on either side of it, slabs *S* of the specimen under investigation. Outside of these layers are other plates cooled by running water, and the whole ensemble is clamped tightly together. For poor conductors where the edge losses may be important, it may be desirable to construct the heater plate in two parts, *A* and *B*, shown in Fig. 53. Each part receives power. The power supply of the part *A* takes care of any losses from the edge and a sufficient part of the specimen so that for the remaining area (equivalent to that of *B*) the equi-temperature surfaces are sensibly plane. The differential thermocouples *ab* and *cd* serve to measure the fall in temperature in the two layers of the material under investigation. The whole assembly may well be packed in some loose insulating material such as diatomaceous earth or rock wool in order to reduce the loss in heat from the edges of *A*.

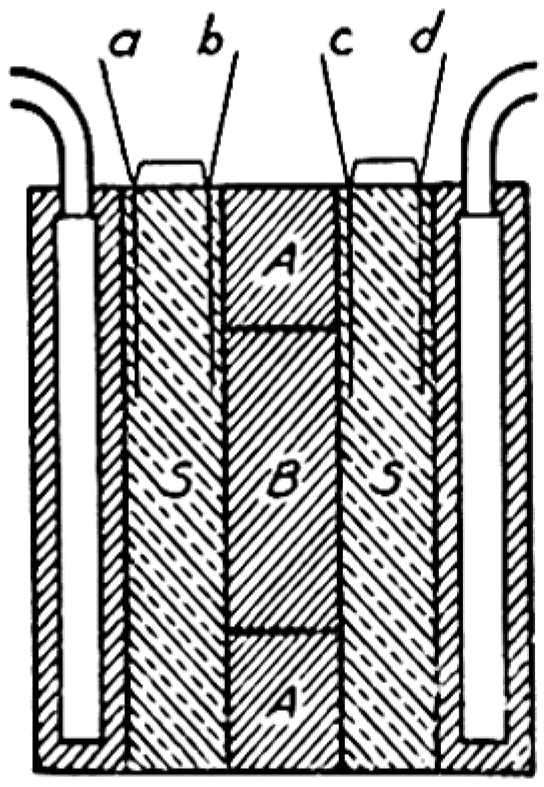

FIG. 53. Parallel plate method for thermal conductivity.

On account of their large conductivity, the fall in temperature across metal plates is likely to be small and therefore difficult to measure with accuracy. It is more satisfactory to use the metal in the form of a rod or bar. The surface of the bar is very thoroughly insulated to prevent losses by radiation and convection. Heat is supplied continuously at a fixed rate at one end of the specimen, and for the steady state the quantity of heat arriving at the other extremity may also be measured. This

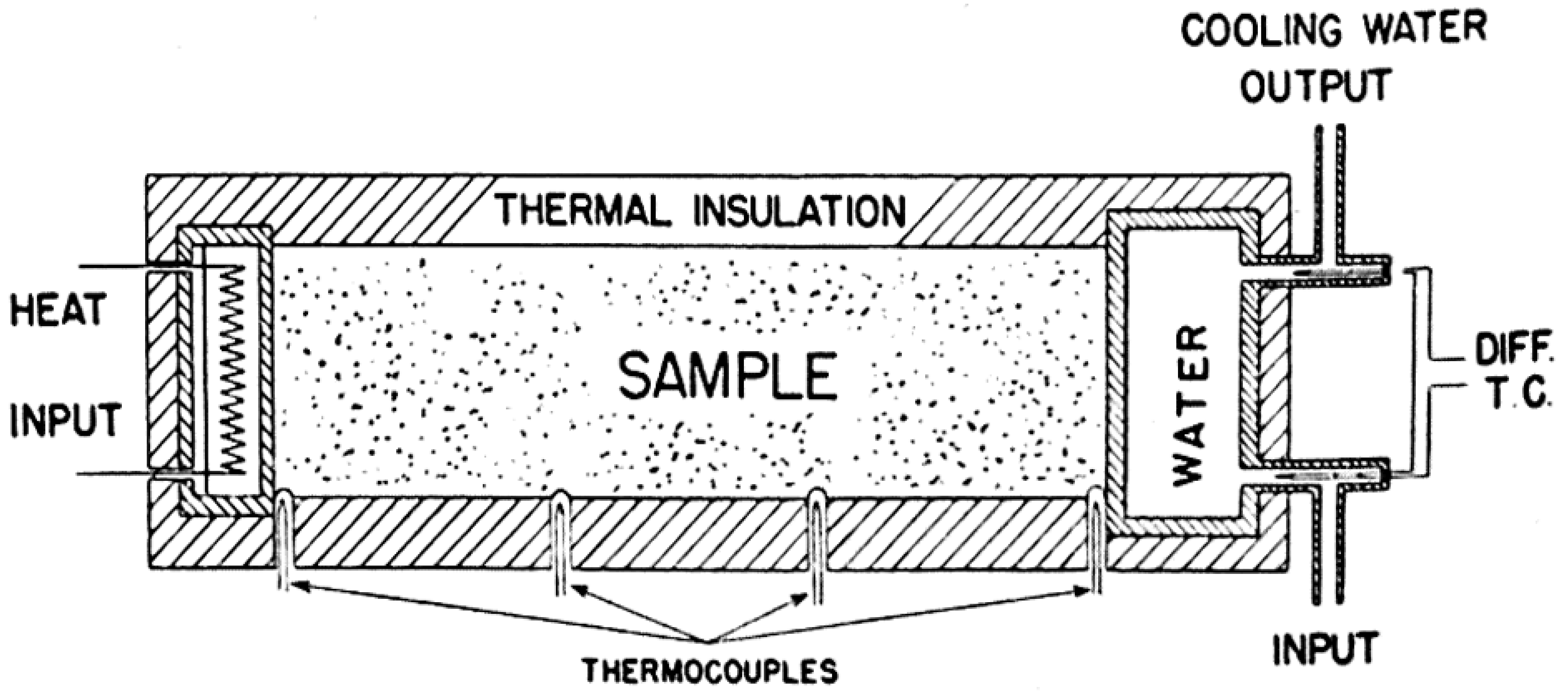

FIG. 54. Thermal conductivity by unidirectional flow along a bar for the steady state.

may be accomplished by observing the change in temperature of a stream of water flowing at a known steady rate through a water-cooled receiver mounted on the end of the specimen and otherwise thermally insulated. The temperature gradient now may be fairly large and is readily measured by thermocouples placed in fine drill holes separated by known distances along the length of the specimen. An arrangement of this sort is shown in Fig. 54.

Thermal Resistance at Contact Surfaces. When heat flows from one medium to another the boundary surface often exerts an important influence on the quantity transferred. It is useful in this connection to define the term thermal resistance, which is equal to the difference in temperature required to cause a flow of heat of one calorie per second. In industrial applications such as heat exchangers, evaporators and radiators the film on a metallic surface may offer a thermal resistance many times that of the metal layer itself. In transfer from metal to metal the quantity of heat conveyed is increased by an increase in pressure squeezing the surfaces together.

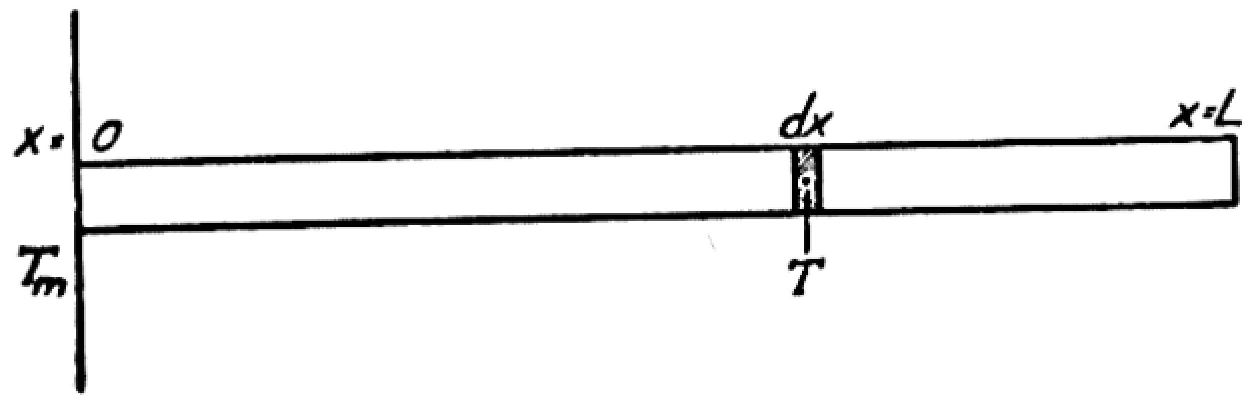

FIG. 55. Flow of heat along a bar heated at one end.

Flow of Heat Along a Bar. Figure 55 represents a bar oriented in the x direction and with the temperature decreasing toward the right as x increases, so that dT/dx is negative. Now at any point along the bar an element of length dx may be chosen at the center of which the temperature is T. Then at the left face of this element the temperature is $T - (\partial T/\partial x) \cdot dx/2$. At the right face the temperature is $T + (\partial T/\partial x) \cdot dx/2$. The inflow of heat per second through the left face is, therefore,

$$\frac{\text{Inflow}}{\text{Second}} = -\kappa A g = -\kappa A \, \frac{\partial\left(T - \dfrac{\partial T}{\partial x} \cdot \dfrac{dx}{2}\right)}{\partial x} \tag{14}$$

and out through the right face is

$$\frac{\text{Outflow}}{\text{Second}} = -\kappa A g = -\kappa A \, \frac{\partial\left(T + \dfrac{\partial T}{\partial x} \cdot \dfrac{dx}{2}\right)}{\partial x} \tag{15}$$

where κ is the thermal conductivity of the material of the bar and A is its sectional area. The excess of the inflow over the outflow of heat is therefore the difference between equations 14 and 15. This quantity of heat either remains in the element of volume, producing there an elevation in temperature per second, $\partial T/\partial t$, or else it is radiated from the surface. If one assumes that the heat loss from the surface obeys Newton's law of cooling and also for the sake of simplicity that the temperature of the surroundings is 0° C., then this difference per second in the inflow and outflow of heat may be written:

$$\kappa A dx \frac{\partial^2 T}{\partial x^2} = A dx \rho (\text{S.H.}) \frac{\partial T}{\partial t} + P \cdot dx \cdot R(T - 0^\circ) \tag{16}$$

In this expression ρ represents the density of the material, S.H. its specific heat, P is the perimeter of the bar, and R denotes the power loss due to radiation from the surface per unit area when the temperature T is 1° above that of the surroundings. By combining constants this may be written:

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{n} \frac{\partial T}{\partial t} + \frac{RP}{\kappa A} \cdot T \tag{17}$$

where n is the diffusivity of the material. For the steady state, that is, $\partial T/\partial t = 0$, the first term of the right-hand member of this equation becomes zero. The second term of this member could be made zero if radiation from the surface were prevented. For the steady state, try as a solution

$$T = Be^{ax} + B'e^{-ax} \tag{18}$$

where B, B', and a are constants to be determined. Other solutions in the form of trigonometric functions are equally applicable. From equation 18, successive differentiation gives

$$\frac{\partial^2 T}{\partial x^2} = Ba^2 e^{ax} + B'a^2 e^{-ax} \tag{19}$$

so that equation 18 is a possible solution if

$$a^2 = \frac{RP}{\kappa A} \tag{20}$$

Now for a particular case, suppose a bar infinitely long maintained at a certain temperature T_m at one end and at 0° C. at the remote end. Then

$$\text{at } x = 0,\ T = T_m, \quad \text{and at} \quad x = \infty,\ T = 0^\circ \text{ C.}$$

Writing these values of T and x in equation 18, it follows that $B=0$ and $B' = T_m$. Hence

$$T = T_m e^{-\sqrt{RP/\kappa A}\cdot x} \tag{21}$$

gives the value of the temperature T at a distance x from the heated end.

Experimental — Method of Ingen-Hausz. A method of comparing the thermal conductivities of various substances was very early developed by Ingen-Hausz.[1] In this experiment the specimens were made in the form of identical rods. They were uniformly coated with wax and heated steadily to a common temperature at one end. It was observed that soon a steady state was attained in which the wax was melted out from the source, different distances on the various rods. If the experimental conditions be approximated as assumed for equation 21, then by measuring the distances on any two of the rods from the source to the respective limits of melted wax, the relative thermal conductivities may be determined. If the distances on the two rods are denoted respectively by l_1 and l_2, then

$$\sqrt{\frac{R_1P_1}{\kappa_1A_1}}\cdot l_1 = \sqrt{\frac{R_2P_2}{\kappa_2A_2}}\cdot l_2 \tag{22}$$

If the rods are made identical in dimensions and radiating power, then

$$\frac{\kappa_1}{\kappa_2} = \frac{l_1^2}{l_2^2} \tag{23}$$

The absolute value of the thermal conductivity may then be found by having one of the rods made of a material for which the conductivity is known. In employing rods of finite length, instead of infinitely long ones as was assumed in equation 21, errors are introduced. These errors are relatively greater the better the conductivity of the material.

Other classical methods to determine relative thermal conductivities were very early described by Despretz[2] and by Wiedemann and Franz.[3]

Experimental — Method of Forbes. An interesting modification of this type of experiment yielding the absolute, rather than the relative, value of the thermal conductivity was employed by Forbes.[4] This experiment consisted of two types of observation. In one, the static, the rod was heated at one end at a constant temperature, until the steady state was attained throughout the entire length. In this condition, the temperatures at various points along the rod were observed, giving a temperature-length relationship as shown graphically in Fig. 56, curve *A*. The other type of observation consisted in heating the rod as a whole to some high temperature and letting it cool. Measurements were made of the rate of cooling so that a temperature-time relationship as shown in Fig. 56, curve *B*, was obtained. Now from curve *A*, the first member of equation 16, except the factor κ, can be evaluated throughout the length of the rod, choosing any arbitrary finite value for *dx*. The first term of the second member is zero, for the steady state. The second member may be evaluated at any temperature *T* by reference to curve *B*. In the cooling experiment the heat radiated comes completely from the internal energy (heat content) of the material of the bar. Thus the energy radiated per second from a section of the rod that is *dx* in length and is at the temperature *T* becomes:

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[1] J. Ingen-Hausz, *Jour. Phys.*, **34**, 68, 380 (1789).

[2] C. Despretz, *Ann. chim. phys.*, **19** [2], 97 (1822).

[3] G. Wiedemann and R. Franz, *Ann. chim. phys.*, **41** [3], 107 (1854).

[4] J. D. Forbes, *Phil. Trans. Roy. Soc. Edinburgh*, **23**, 133 (1862).

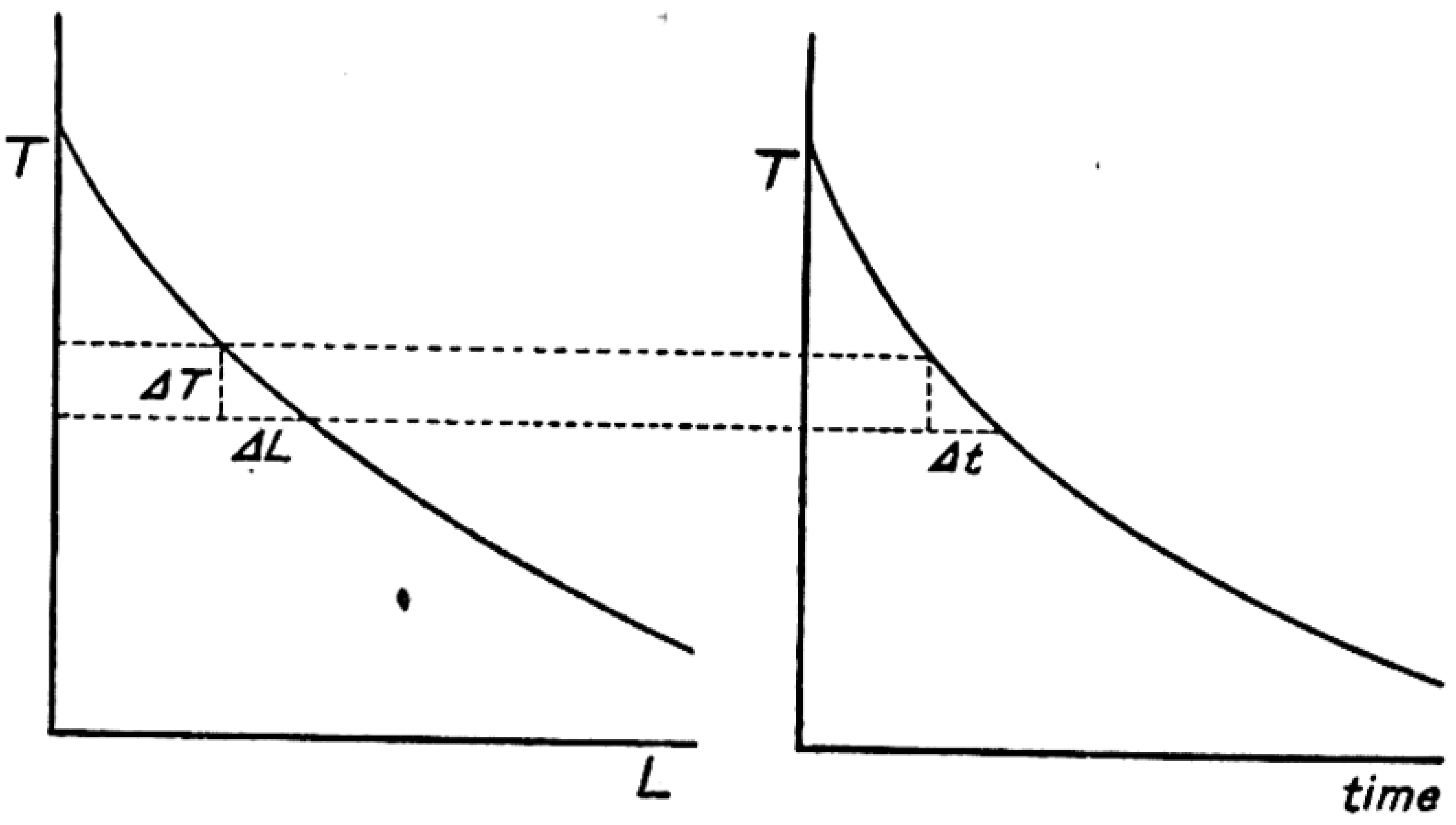

FIG. 56. Curves for the determination of thermal conductivity by the method of Forbes.

$$R \cdot P \cdot dx \cdot T = A \cdot dx \cdot \rho(S.H.)\frac{\partial T}{\partial t} = \kappa A \frac{\partial g}{\partial x} \cdot dx \qquad (24)$$

The temperature gradient g is $\partial T/\partial x$, so that $\partial g/\partial x$ represents $\partial^2 T/\partial x^2$ in equation 16. From this:

$$\kappa = \rho(\text{S.H.}) \frac{\partial T/\partial t}{\partial g/\partial x} \qquad (25)$$

The quantity $\partial g/\partial x$ is obtained graphically from curve *A*, by observing the change in slope for two neighboring points in the bar and dividing this difference by the distance between the points. $\partial T/\partial t$ is the slope of curve *B* at the particular average temperature used to obtain $\partial g/\partial x$. By choosing *dx* at different positions along the bar, any variation of the thermal conductivity with the temperature may be observed.

The Periodic Flow of Heat in One Direction. It often happens that heat is applied with a certain periodicity to the surface of a body. It may be desired to find at what rate this disturbance is transmitted through the material. If the body is sufficiently large the surface may be regarded as a plane. Such, for example, is the sun's action on the surface of the earth. By choosing the x axis normal to the surface, the flow in both the y and z directions will be zero. A similar case might be a uniform rod with the cylindrical surface thermally insulated and subjected to a periodic heating at one end, while the other end at a distance l is at some lower temperature. For the one-dimensional steady state, the temperature gradient g was shown in equation 11 to be constant, so that if T_H is the temperature at the heated end, where $x = 0$, then at any other position x, the steady temperature would be T_H minus $x \cdot g$.

By superimposing upon this distribution a periodic heating at the hotter end, whose variation can be represented by a cosine or sine function, a disturbance will travel along the bar. This boundary condition may be stated as follows: at $x = 0$, $T = T_H + \Delta T = T_H + T_m \sin \omega t$ where T_m is the maximum amplitude of the variation in temperature and ω is 2π times the frequency f of the periodic heating. Equation 8 may be written for the case of unidirectional flow as

$$\frac{\partial^2 T}{\partial x^2} = \frac{\rho(\text{S.H.})}{\kappa} \cdot \frac{\partial T}{\partial t} = \frac{1}{n} \cdot \frac{\partial T}{\partial t} \tag{26}$$

where n is written for the diffusivity. Particular solutions that satisfy this equation may be found by the method of trial.

Since the amplitude of the periodic wave might be expected to be damped logarithmically as x increases and this be superimposed on the steady state, it would be reasonable to try a solution as

$$T = T_H - g \cdot x + ce^{ax} \sin (\omega t + bx) \tag{27}$$

where a, b, and c are constants. T is the temperature at the time t, of any point at a position x, and e is the natural logarithmic base. Then on differentiation

$$\frac{\partial T}{\partial t} = c\omega e^{ax} \cos (\omega t + bx) \tag{28}$$

and

$$\frac{\partial T}{\partial x} = -g + ace^{ax} \sin (\omega t + bx) + bce^{ax} \cos (\omega t + bx) \tag{29}$$

from which

$$\frac{\partial^2 T}{\partial x^2} = a^2ce^{ax}\sin(\omega t + bx) - b^2ce^{ax}\sin(\omega t + bx) + 2abce^{ax}\cos(\omega t + bx) \tag{30}$$

On substituting the expressions of equations 28 and 30 into equation 26 an identity results if

$$a^2 = b^2 \text{ and } 2ab = \frac{\omega}{n} \quad \text{or} \quad a = \pm b = \pm\sqrt{\frac{\omega}{2n}}$$

Since the amplitude of the variation in temperature decreases as the distance from the disturbance increases, the negative sign is chosen for a.

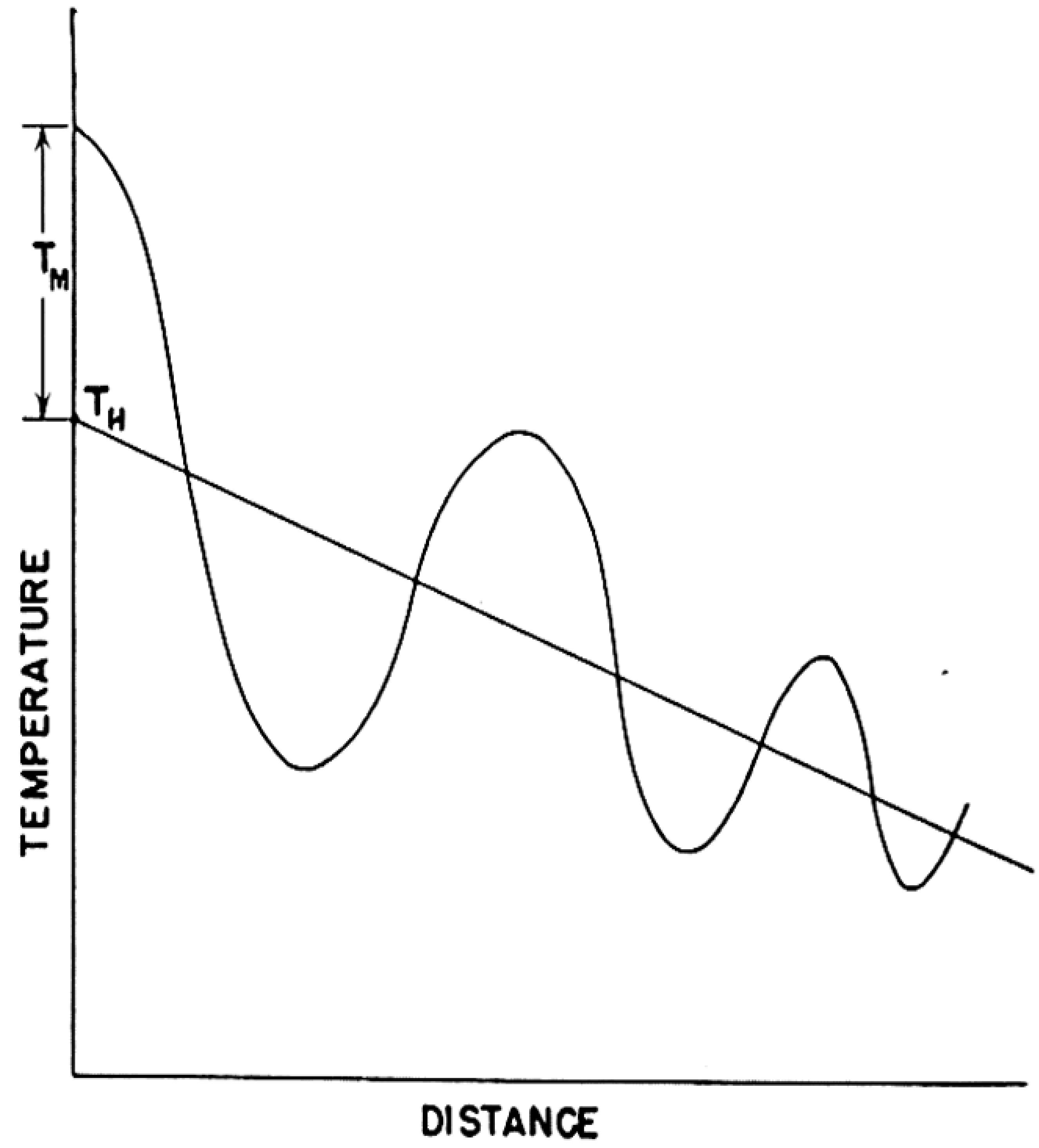

FIG. 57. Instantaneous distribution of temperature, method of periodic flow.

The constant c is also the amplitude T_m. Hence a satisfactory solution is

$$T = T_H - g \cdot x + T_m e^{-x\sqrt{\omega/2n}} \sin\left(\omega t - x\sqrt{\frac{\omega}{2n}}\right) \tag{31}$$

Such a distribution of temperature at a particular instant is shown in Fig. 57.

At any point x the temperature will have a maximum value when

$$\sin\left(\omega t - x\sqrt{\frac{\omega}{2n}}\right) = 1 \tag{32}$$

If the distance between successive maxima, corresponding to a wavelength, is represented by λ, then at any instant

$$\left[\omega t - x\sqrt{\frac{\omega}{2n}}\right] - \left[\omega t - (x + \lambda)\sqrt{\frac{\omega}{2n}}\right] = 2\pi = \lambda\sqrt{\frac{\omega}{2n}} \tag{33}$$

whence

$$n = \frac{\omega\lambda^2}{8\pi^2} = \frac{f\lambda^2}{4\pi} = \frac{\lambda^2}{4\pi P} = \frac{\kappa}{(\text{S.H.})\rho} \tag{34}$$

Thus a measurement of λ, the distance between two successive maxima and P, the period of the heating, gives readily the value of the diffusivity, from which the conductivity κ may be deduced.

This relationship shows that the diffusivity is related to the velocity of propagation of the heat wave. The velocity is λ/P and hence is

$$v = \frac{\lambda}{P} = \frac{\kappa}{(\text{S.H.})\rho} \cdot \frac{4\pi}{\lambda} = \frac{4\pi n}{\lambda} = \sqrt{\frac{4\pi n}{P}} \tag{35}$$

This pertains to the velocity with which a maximum or minimum will travel through the medium and does not apply to the speed with which energy is transmitted from particle to particle. Likewise the time t for the maximum to travel any distance x may be readily found as follows:

$$t = \frac{x}{v} = x\sqrt{\frac{P}{4\pi n}} \tag{36}$$

As an illustration, results may be calculated for periodic waves in soil at the surface of the earth. An approximate value for the diffusivity n of soil is 0.005 cm.^{2} sec.$^{-1}$. Hence the velocity of propagation for the diurnal wave into the surface is:

$$v = \sqrt{\frac{4\pi(0.005)}{86{,}400}} = 8.528 \times 10^{-4} \text{ cm. per sec.}$$

The time required for a maximum to travel to a depth of 1 meter would then be 32.5 hours.

For the annual wave the velocity may be shown to be 4.464×10^{-5} cm. per sec. and the time for the maximum to arrive at a depth of 1 meter would be 25.9 days.

Experimental — Periodic Flow. One of the earliest experimenters to determine the thermal conductivity of a specimen by the method of the periodic flow of heat was Ångström.[5] In modified form this method has been used by many later investigators.[6] A very satisfactory arrangement suitable as a laboratory experiment is shown in Fig. 58. The bar being tested has its surface thermally insulated and is heated at one end by an electric coil *H*.

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[5] A. J. Ångström, *Phil. Mag.*, **25**, 130 (1863).

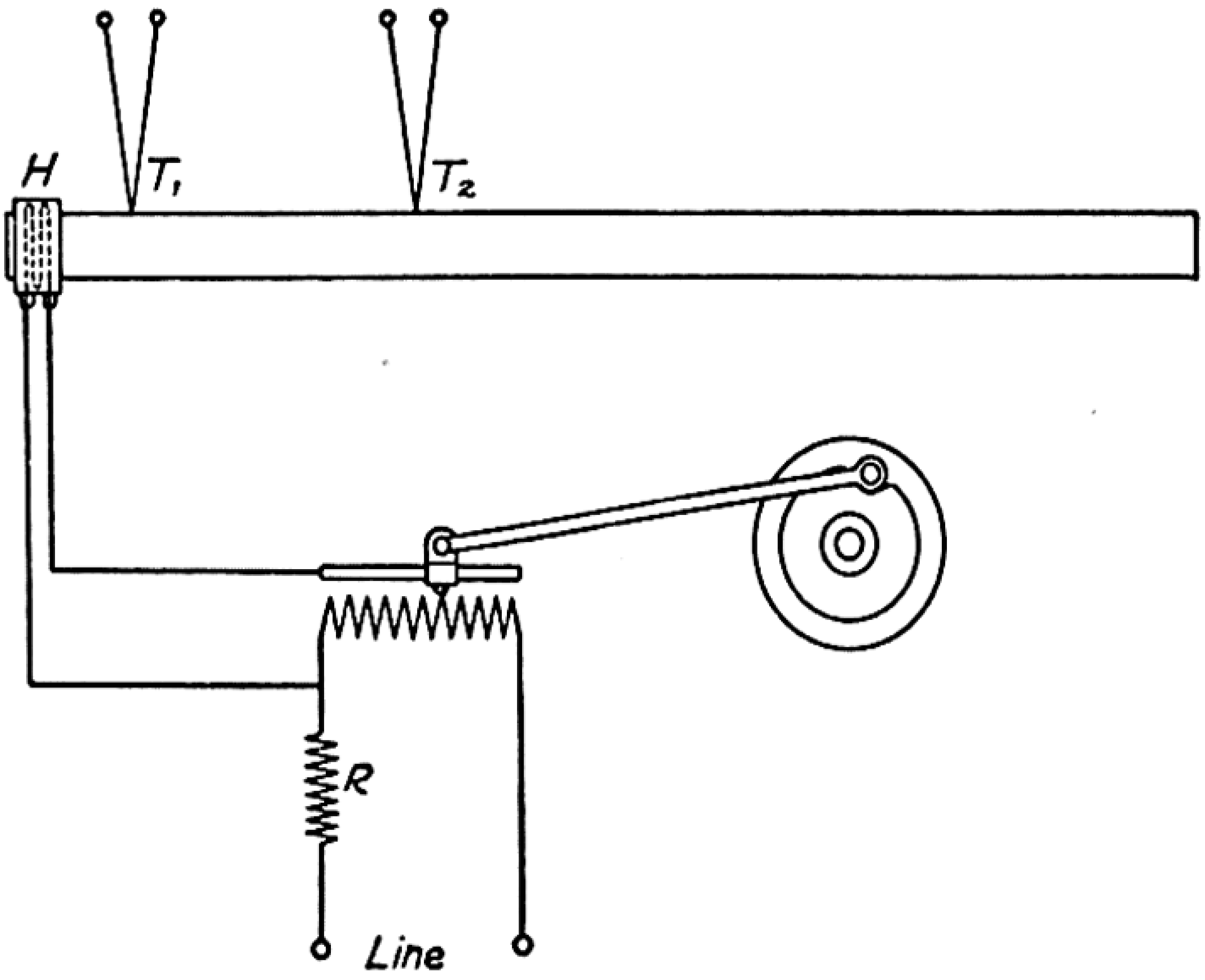

FIG. 58. Apparatus for determining thermal conductivity by the method of periodic flow.

The current through this heater coil is varied by the automatic harmonic motion of a sliding contact on a resistance, across which the line voltage is applied. The thermocouples T_1 and T_2 are placed in drill holes spaced a definite known distance apart. Each thermocouple is connected to a galvanometer and the deflection of each is recorded every half minute over a sufficiently long time to include a few heating cycles. Since, if connected directly, the thermocouple would make the galvanometer deflect off scale, a potentiometric arrangement may be employed to counteract most of the developed electromotive force. This will keep the readings on the scale and retain the high sensitivity of the galvanometer.

From the graphical recordings of the deflections and the corresponding times at each station, it is possible to express the time required for the wave to travel the intervening distance. The distance divided by the time yields the desired velocity *v*, which, combined with the period *P* of the heating cycle, gives the thermal conductivity. This may be stated explicitly from equation 34 as

$$\kappa = \frac{1}{4\pi} v^2 (\text{S.H.}) \rho P \tag{37}$$

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[6] H. L. Callendar, *Encyclopaedia Britannica*, Fourteenth Edition, Vol. 11, p. 328; R. W. King, *Phys. Rev.*, 6, 407 (1915).

Spherical Flow, Steady State. In the flow of heat where equitemperature surfaces are spherical in form, the general differential equation 8 may be transformed to spherical coordinates and solutions obtained for certain particular cases. For the steady state, which is perhaps the most common in actual practice, this task may be greatly simplified as follows: Fig. 59 represents a section of a spherical shell whose inner and outer radii are r_1 and r_2, respectively. The inner surface of the shell is maintained uniformly at the temperature T_1, while the temperature of the outer surface is represented by T_2. For the steady state, the flow of heat across any of the infinite number of concentric spherical shells of radius r inscribed in the body must be constant. The temperature gradient is $\partial T/\partial r$, so that the quantity of heat flowing per second is:

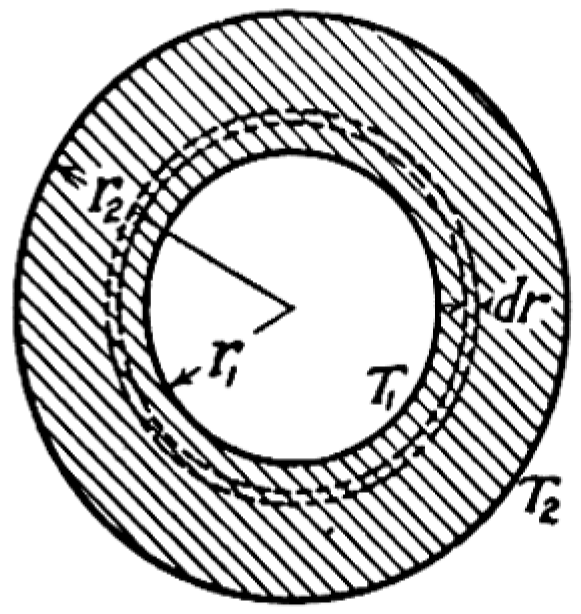

FIG. 59. Section of thermal conductor in the form of a spherical shell.

$$-\kappa A' g = -4\pi r^2 \frac{\partial T}{\partial r}\cdot \kappa = (\text{Constant})\; c \tag{38}$$

By separating the variables r and T and integrating,

$$T = \frac{A}{r} + B \tag{39}$$

where A and B are integration constants to be determined. From the boundary conditions that $T = T_1$ for $r = r_1$ and $T = T_2$ for $r = r_2$, it follows that

$$A = \frac{T_1 - T_2}{r_2 - r_1} r_1 r_2 \quad \text{and} \quad B = \frac{r_2 T_2 - r_1 T_1}{r_2 - r_1} \tag{40}$$

Hence equation 39 becomes

$$T = \frac{T_1 - T_2}{r_2 - r_1}\cdot\frac{r_1 r_2}{r} + \frac{r_2 T_2 - r_1 T_1}{r_2 - r_1} \tag{41}$$

This represents the temperature T at any point in the spherical shell, at a distance r from the center.

Experimental — Spherical Flow. An electric heater may be placed at the center of the inner spherical cavity shown in Fig. 59. If power be supplied at a constant known rate for a sufficiently long time for the temperatures of the inner and outer walls to attain equilibrium, then equations 38–41 for the steady state are applicable. The difference in temperature between inner and outer spheres may easily be measured by a calibrated differential thermocouple. It follows therefore, by differentiating equation 41 to obtain $\partial T/\partial r$, that the energy supplied per second $EI/J \left(\frac{\text{calories}}{\text{second}}\right)$ is equivalent to

$$\frac{EI}{J} = -\kappa A' \frac{\partial T}{\partial r} = \kappa \cdot 4\pi r^2 \cdot \frac{T_1 - T_2}{r_2 - r_1} \cdot \frac{r_1 r_2}{r^2} \tag{42}$$

Hence

$$\kappa = \frac{EI(r_2 - r_1)}{4\pi J r_1 r_2 (T_1 - T_2)} \tag{43}$$

All the quantities of the right member are measurable.

Cylindrical Flow, Steady State. When the flow of heat occurs with equitemperature surfaces that are cylindrical in form, an equation applicable to the steady state may be very simply obtained. Arrangements of this sort are indeed very common in practice, such as the flow of heat through the insulated covering of steam pipes. Figure 59 equally well represents a perpendicular section of such a cylindrical shell. The inner surface whose radius is r_1 is maintained uniformly at the temperature T_1 while the outer surface of radius r_2 assumes the constant temperature T_2. For the steady state the total flow of heat per second through any of the infinite number of concentric cylindrical layers of radii greater than r_1 and less than r_2 must be the same. A sectional view through the length of the cylinder is shown in Fig. 60.

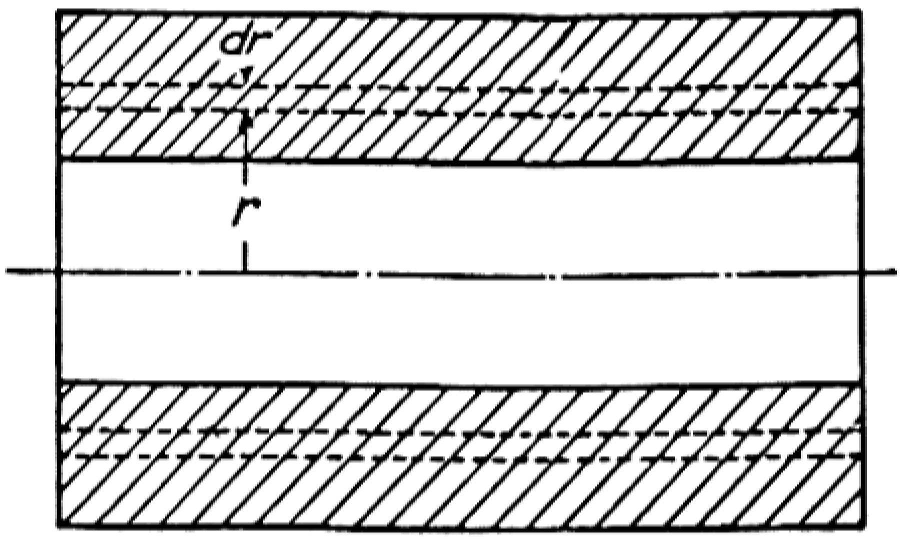

FIG. 60. Longitudinal section of thermal conductor in the form of a cylindrical shell.

The flow in energy per second outward through the cylindrical surface of a section whose length is l is

$$\frac{Q}{t} = -\kappa A' g = -\kappa(2\pi r) \cdot l \cdot \frac{\partial T}{\partial r} = (\text{Constant})\ c \tag{44}$$

The temperature gradient is represented by $\partial T/\partial r$. By the separation of the variables r and T, and integration, it follows that

$$T = A \log_e r + B \tag{45}$$

where A and B are again constants of integration to be determined. From the boundary conditions that, at $r = r_1$, $T = T_1$, and for $r = r_2$,

$T = T_2$, it follows that

$$A = \frac{T_1 - T_2}{\log_e r_1/r_2} \quad \text{and} \quad B = \frac{T_2 \log r_1 - T_1 \log r_2}{\log_e r_1/r_2} \tag{46}$$

These values when substituted in equation 45 give

$$T = \frac{T_1 - T_2}{\log_e r_1/r_2} \cdot \log_e r + \frac{T_2 \log r_1 - T_1 \log r_2}{\log_e r_1/r_2} \tag{47}$$

This is the general expression for the temperature T at any point in the cylindrical shell at a distance r from the axis.

Experimental — Cylindrical Flow. Consider a linear heater coil placed along the axis of the inner cylinder of length l in Fig. 60. If the power per unit length is maintained constant at some known value, then the inner and outer surfaces of the shell of material will attain certain equilibrium temperatures. The difference between these two temperatures may be most easily obtained by the use of a calibrated differential thermocouple.

It follows then for the steady state, by differentiation of equation 47, that the loss in heat expressed in calories per second per unit length of cylinder is

$$\begin{aligned} \frac{EI}{Jl} &= -\kappa A' g = -\kappa \cdot 2\pi r \cdot \frac{\partial T}{\partial r} \\ &= \kappa \cdot 2\pi r \cdot \frac{T_1 - T_2}{\log_e r_2 - \log_e r_1} \cdot \frac{1}{r} \end{aligned} \tag{48}$$

From this

$$\kappa = \frac{EI \log_e (r_2/r_1)}{2\pi Jl(T_1 - T_2)} \tag{49}$$

All the quantities of the right member are easily determined experimentally.

The Method of Cylindrical Flow in Metals. Many other modifications[7] of the method of cylindrical flow have been used to determine thermal conductivity. In certain of these, the specimen is an electric conductor in cylindrical form and is heated by carrying a constant electric current. If the cylindrical conductor is sufficiently long the cooling of the ends is not significant at the central section. In this case the axis will become warmer than the outer surface. The heat flow is therefore radially outward with cylindrical symmetry. In the steady state the total heat developed electrically within a short cylinder of radius r must all be transmitted through the outer surface A of that cylinder. If i denotes the current density and $\mathcal{E}$ the fall in electric potential per centimeter, then for a cylinder of length dx this quantity of heat per second is

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[7] M. F. Angell, *Phys. Rev.*, **33**, 421 (1911); A. G. Worthing, *Phys. Rev.*, **4**, 535 (1914); I. Langmuir, *Phys. Rev.*, **7**, 151 (1916).

$$\frac{\mathcal{E}i}{J} \cdot \pi r^2 \cdot dx = -\kappa A g = -\kappa \cdot 2\pi r dx \frac{\partial T}{\partial r} \qquad (50)$$

where κ is the thermal conductivity of the metal. Upon separating the variables and integrating, this becomes:

$$r dr = \frac{-2\kappa J}{\mathcal{E}i} \cdot dT \quad \text{and} \quad -r^2 = \frac{4J\kappa}{\mathcal{E}i} \cdot T + a \qquad (51)$$

where a is a constant of integration. In the actual experiment the temperature is measured both at the axis of the central section T_c and at the surface T_0. For these limits, $T = T_c$ at $r = 0$ and $T = T_0$ at $r = R$, the integration constant a disappears giving

$$\kappa = \frac{\mathcal{E}iR^2}{4J(T_c - T_0)} \qquad (52)$$

In practice the cylinder may have an axial drill hole throughout its entire length so as to accommodate a thermocouple. A slight alteration in the formula may be made to allow for the variation in the resistivity of the metal with temperature, so that i is not constant with r.

Thermal Conductivity, Electrical Conductivity, and Temperature. It was very early observed by Wiedemann and Franz[8] from their results on the thermal conductivities of metals that those substances which were good thermal conductors were also good electrical conductors. This relationship between thermal and electrical conductivities has been the subject of many subsequent investigations.[9] The conclusion which may be drawn from these experiments, known as the Wiedemann-Franz law, may be summarized as follows: "The ratio of the thermal to the electrical conductivity for all pure metals has the same value at any given temperature, and the value of this ratio for any particular metal varies directly as the absolute temperature."

The mechanism by which heat is transferred in the process of conduction is somewhat problematical. Debye[10] has pointed out that, in a crystalline solid, if the particles associated with the lattice points obey Hooke's law, then an infinite thermal conductivity as well as an infinite value for the velocity of sound should be expected. If instead of Hooke's law, another law be allowed in which a greater force is needed to bring the atoms together than to separate them, then many phenomena should follow as observed, such as a positive coefficient of expansion and a finite coefficient of thermal conductivity.

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[8] G. Wiedemann and R. Franz, *Pogg. Ann.*, **89**, 497 (1853); *Ann. chim.*, **41** [3], 107 (1854).

[9] W. Jaeger and H. Diesselhorst, *Abh. phys. tech. Reich.*, **3**, 269 (1900); W. Meissner, *Ber. deut. phys. Ges.*, **12**, 262 (1914); C. H. Lees, *Roy. Soc., Phil. Trans.*, **208** ,381 (1908).

The possibility of accounting for the conduction of heat by attributing it to the free conductivity electrons was first suggested by Drude.[11] This theory has been elaborated by many later investigators. Free electrons are assumed to exist at all times in the metal. According to the theory of Drude, each electron is to be regarded as if it were a mass point. It thus behaves like a particle of gas, and hence at a given temperature T it possesses the average kinetic energy $\frac{3}{2}kT$, where k denotes the gas constant per molecule. The electron, by its collision with atomic particles, along with the consequent interchange of energy, is an important factor in establishing thermal equilibrium. The life of an electron is to be regarded as the period elapsing between the time it is dislodged from a normal atom until its impact with another atom to which it attaches itself. In the absence of electric fields and temperature gradients, there exists a purely random motion such that there is no net flow of either energy or electric charge across any area during the finite interval of time.

Electrical Conductivity. By applying an electric field $\mathfrak{E}$ to the metal, every electron of electric charge $(-e)$ will be acted upon by a force F equal to $(-\mathfrak{E}e)$. This force may act so as either to increase or decrease the magnitude of the velocity of the electron. It will in general superimpose upon any original velocity V a drift velocity $\bar{v}$ counter to the field, and equal to $\frac{1}{2}$ the maximum change in velocity ΔV acquired during the life of the electron. The term V represents the average life velocity of an electron. The life of the electron is the time required for it to travel the distance of its mean free path since on impact it does not rebound elastically. Thus

$$v = \frac{\Delta V}{2} = \frac{1}{2}at = \frac{1}{2}\cdot\frac{F}{m}\cdot\frac{l}{V} = \frac{1}{2}\frac{\mathfrak{E}e}{m}\cdot\frac{l}{V} \tag{53}$$

where m denotes the mass of the electron and a is the acceleration imparted to it by the electric field. Now if N denotes the number of free electrons per cubic centimeter, then $N\bar{v}$ would denote the number of electrons which would move across any unit area normal to $\mathcal{E}$, per second, because of the electric field. As each electron carries the charge e then the current density i or the electric charge q per square centimeter per second is

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[10] P. Debye, Vortrag, Wolfskehl-Kongress, zu Göttingen, 1913.

[11] P. Drude, *Ann. Physik,* **1,** 566 (1900); H. A. Lorentz, *Theory of Electrons,* 1909.

$$i = \frac{q}{At} = N\bar{v}e = \frac{\mathcal{E}e^2}{2m} \cdot \frac{Nl}{V} \tag{54}$$

But from Ohm's law, where ρ denotes the electrical resistivity and σ the electrical conductivity, the current density i is:

$$i = \frac{\mathcal{E}}{\rho} = \mathcal{E}\sigma = \frac{1}{2}\frac{\mathcal{E}e^2}{m} \cdot \frac{Nl}{V} \tag{55}$$

Rewriting after multiplying the numerator and denominator by V and replacing the expression for the average K.E. ($\frac{1}{2}mV^2$) by $\frac{3}{2}kT$, one has for the electrical conductivity:

$$\text{(Elec. Cond.) } \sigma = \frac{e^2}{2m} \cdot \frac{Nl}{V} = \frac{e^2}{4} \cdot \frac{NlV}{\frac{1}{2}mV^2} = \frac{e^2}{6k} \cdot \frac{NlV}{T} \tag{56}$$

It may be observed that since the electrical conductivity is experimentally found to be inversely proportional to T then the product NlV must be independent of the temperature. From kinetic theory it must follow that V varies as $\sqrt{T}$. The number of free electrons per cubic centimeter was generally regarded in early theories[12] to increase as $\sqrt{T}$. Hence it should follow that l varies linearly with $1/T$. The state of superconductivity in the metals must then be identified as one with very long mean free paths for the electrons. This may perhaps be better expressed as a state of greatly reduced stopping power of the lattice particles for moving electrons. This is what should be expected if the stopping power of the atom is inherent in the electrical polarization produced by the heat motion.

In the more recent theory of Sommerfeld[13] the value of N is supposed to be of the same order of magnitude as the number of metallic atoms per cubic centimeter, and to a first approximation the velocity of the electrons is independent of the temperature.

Thermal Conductivity. Let us choose any equitemperature surface in the bar having a temperature T as shown in Fig. 61, where temperatures at the left are greater and those at the right are less than T. Now the N electrons per cubic centimeter may be regarded as in equilibrium with the particles of the metal, hence they possess an average kinetic energy $\frac{3}{2}kT$. Also like gas particles the effective component of velocity in one direction such as V_x along the x axis obeys the relationship:

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[12] J. J. Thomson, *The Corpuscular Theory of Matter*, p. 80, 1907.

[13] A. Sommerfeld, *Zeit. Phys.*, **47**, 1928, *et seq.*

$$\tfrac{1}{3}V^2 = V_x^2 \tag{57}$$

and since a velocity to the right is as probable as one to the left, therefore from each cubic centimeter $N/2$ of the particles would move toward the right and $N/2$ toward the left. Through any equitemperature surface, there will stream in each second a column of particles numerically equal in length to the velocity V_x. Therefore in each second through a square centimeter from left to right would pass $(N/2)(V/\sqrt{3})$ electrons. Now these electrons in passing from left to right are moving from a higher to a lower temperature and each travels on the average during its life the distance l', where l' is the component of the mean free path in a direction parallel to x. The mean free path l has a random distribution and its effective component in the x direction, shown as l' in Fig. 61 is $l/\sqrt{3}$. Each electron therefore, coming from a distance l' on the left, possesses an energy $\frac{3k}{2}\left(T - \frac{\partial T}{\partial x}\cdot\frac{l}{\sqrt{3}}\right)$. Now for an equivalent electron coming from a distance l' on the right the energy is $\frac{3k}{2}\left(T + \frac{\partial T}{\partial x}\cdot\frac{l}{\sqrt{3}}\right)$. Since there is no continued accumulation of charge in any part of the conductor as many electrons per second must pass toward the right as pass toward the left. The net gain in the transfer of energy from left to right for each pair of electrons is therefore:

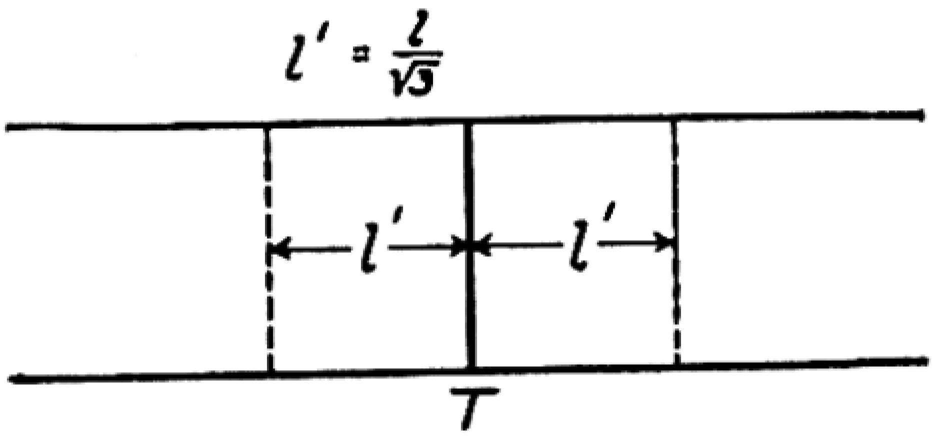

FIG. 61. Section of thermal conductor for demonstrating conduction by free electrons.

$$\text{Energy transfer per pair of electrons} = \sqrt{3}\cdot k\cdot l\cdot\frac{\partial T}{\partial x} \tag{58}$$

The total number of electrons arriving from the left or from the right per square centimeter is:

$$\frac{NV}{2\sqrt{3}} \text{ per second}$$

Hence the net flow of energy left to right per second is:

$$\frac{NV}{2\sqrt{3}}\cdot\sqrt{3}kl\frac{\partial T}{\partial x}$$

This may be set equal to the usual expression for the heat transferred by the thermal conductivity κ, giving per square centimeter per second

$$-\kappa g = \frac{k}{2} \cdot NVl \cdot \frac{\partial T}{\partial x} \tag{59}$$

Hence

$$\kappa = \frac{k}{2} \cdot NVl \tag{60}$$

The product NVl appearing in equation 55 was independent of temperature. Hence the thermal conductivity κ would be expected to be constant with respect to changes in the temperature T. This has been reported to be true for many pure metals, for temperatures from −170° C. to 20° C. At higher temperatures some metals, particularly alloys, show an increased conductivity, whereas in certain cases a decreased conductivity has been observed.

Ratio of Thermal and Electrical Conductivities. Dividing equation 60 by 57 it follows that

$$\frac{\kappa}{\sigma} = 3\,\frac{k^2}{e^2} \cdot T \tag{61}$$

This is a formulation of the Wiedemann-Franz law. The value of the numerical constant varies somewhat with the method of development. In this development no distinction has been made between average velocity and the effective velocity. The development of Lorentz allowing for the Maxwellian distribution of velocities leads to the identical expression except that the numerical value of the constant is 2 instead of 3. Agreeing best with experimental results is a value between 3 and 3.5. The development by Sommerfeld has given for this constant the value 3.3. This development also explains satisfactorily the absence of a contribution by the free conduction electrons to the specific heat of the metal.

The best values for κ and σ for the common metallic elements are shown collectively in Table 7.

It is observed that the average value of $\kappa/\sigma T$ in joules sec.^{-1} ohm $(\text{deg. C.})^{-2}$ is 2.34×10^{-8}. This may be compared with the calculation from $3k^2/e^2$ which gives 3.04×10^{-8} in the same units.

Experimental. In a quite simple way the value of this ratio $\kappa/\sigma T$ may be determined directly by experiment. The following description illustrates a possible method. The specimen under investigation is in the form of a rod of sectional area A and held in heavy water-cooled mountings at each end as shown in Fig. 62*A*. Losses of heat from the surface of the bar are avoided by covering the bar with a

TABLE 7

THE THERMAL CONDUCTIVITY κ, ELECTRICAL RESISTIVITY $1/\sigma$ AND THE RATIO THERMAL (κ)/ELECTRICAL (σ) × TEMPERATURE (T) OF THE COMMON METALS AT 0° C.

Substance		Thermal Conductivity (κ) Joules cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$	Electrical Resistivity (1/σ) Ohm cm. × 10^6	$\frac{\kappa \cdot 10^8}{\sigma T}$
Name	Symbol			
Silver	Ag	4.19	1.55	2.38
Aluminum	Al	2.03	2.62	1.95
Gold	Au	2.96	2.19	2.38
Bismuth	Bi	0.0837	106.5	3.25
Graphite	C	0.157	1375.	(79.00)
Cadmium	Cd	0.933	6.83	2.34
Cobalt	Co	0.690	5.595	1.42
Copper	Cu	3.88	1.64	2.39
Iron	Fe	0.685	8.53	2.14
Mercury	Hg	0.0836	94.07	2.88
Iridium	Ir	0.59	6.08	1.33
Potassium	K	0.99	6.15	2.24
Lithium	Li	0.70	8.55	2.20
Magnesium	Mg	1.55	4.27	2.42
Molybdenum	Mo	1.46	5.14	2.75
Sodium	Na	1.35	4.2	2.08
Nickel	Ni	0.586	6.93	1.49
Lead	Pb	0.352	19.8	2.56
Palladium	Pd	0.674	10.0	2.46
Platinum	Pt	0.695	9.93	2.50
Rhodium	Rh	0.894	4.70	1.56
Antimony	Sb	0.186	39.0	2.66
Tin	Sn	0.657	10.48	2.52
Tantalum	Ta	0.544	15.2	3.02
Thallium	Tl	0.39	17.65	2.52
Tungsten	W	1.60	5.00	2.93
Zinc	Zn	1.13	5.64	2.34
			Average Value	2.34

sufficiently thick layer of insulating material. Now if a constant current be sent through the rod until the steady state is attained, then, by the cooling at the ends, equitemperature surfaces will be normal to the length of the rod, and the flow of heat will be toward each end.

For any element of volume, dx in length and of sectional area A, then $\kappa \cdot A \cdot dx\, \partial^2 T/\partial x^2$ represents the excess of the inflow of heat over the outflow, or vice versa, per second. For the steady state and in the absence of any loss in heat from the surface this difference in the quantity of heat is represented by the heat developed electrically in the volume. If $\mathfrak{E}$ is the voltage fall per centimeter and i is the current density, then $\mathfrak{E}i$ means the electrical energy spent per cubic centimeter per second. But $i = \mathfrak{E}\sigma$ by Ohm's law, and $\mathfrak{E} = \partial V/dx$.

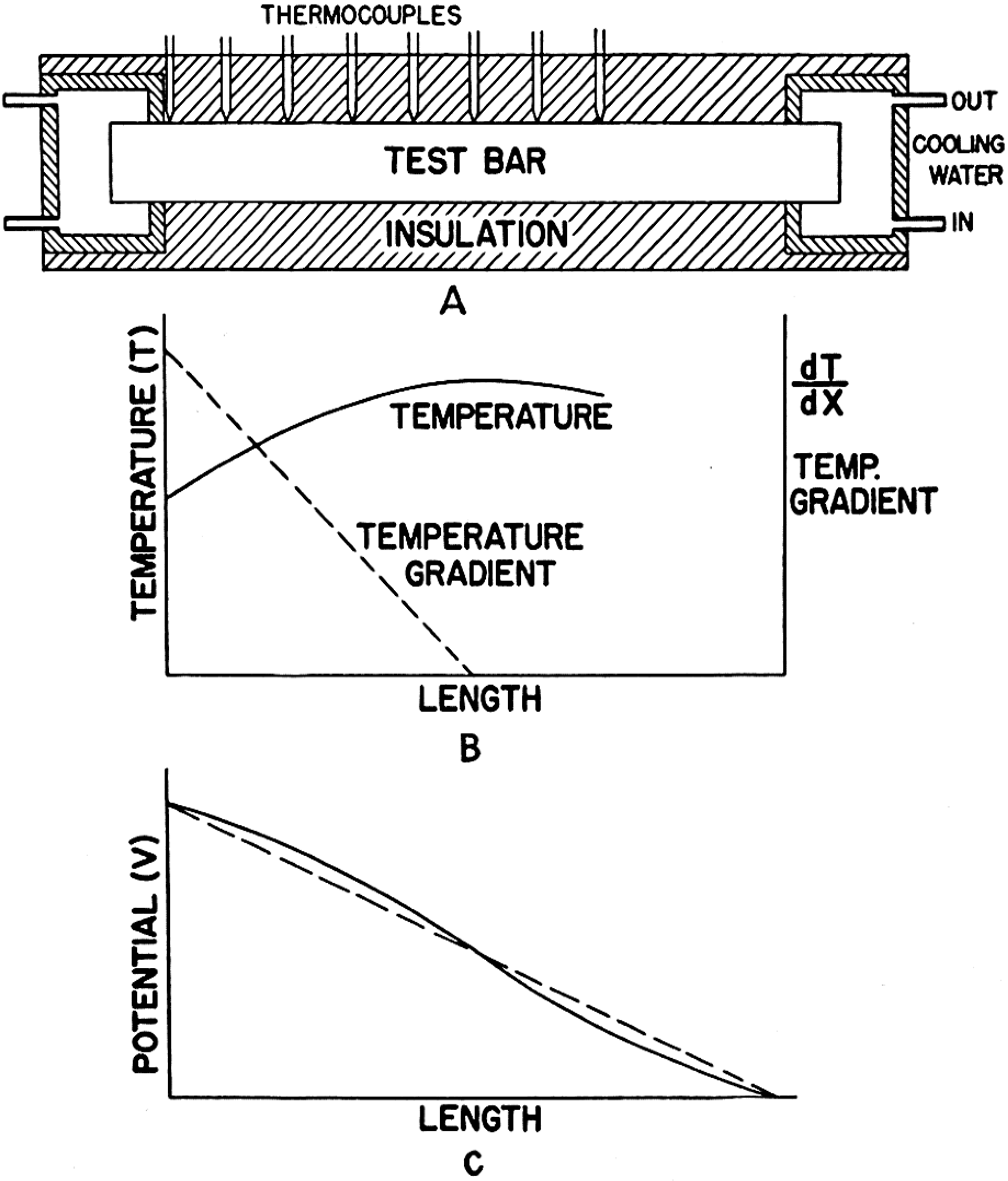

FIG. 62. The experimental determination of the ratio of thermal to electrical conductivities: *A*. Sectional view of conducting material. *B*. Temperature distribution. *C*. Electrical potential distribution.

Hence these energies per second may be expressed as

$$A \cdot dx \cdot \frac{\mathfrak{E}i}{J} = \kappa A dx \cdot \frac{\partial^2 T}{\partial x^2} \tag{62}$$

which becomes

$$\frac{\sigma \mathcal{E}^2}{J} = \kappa \frac{\partial^2 T}{\partial x^2} \tag{63}$$

so that

$$\frac{\kappa}{\sigma} = \frac{\mathcal{E}^2}{J \dfrac{\partial^2 T}{\partial x^2}} = \frac{\left(\dfrac{\partial V}{\partial x}\right)^2}{J \dfrac{\partial^2 T}{\partial x^2}} \tag{64}$$

A potentiometer provided with a multiple contact dial switch is connected in rapid succession with each thermocouple, so that the temperature distribution for the steady state, as shown in Fig. 62*B*, is obtained. The slope of this curve is the temperature gradient g shown plotted as the dotted line in the same figure. The negative slope of the dotted gradient line is the $\partial^2 T/\partial x^2$ in the denominator of equation 64. The potential distribution for the steady state is found by connecting one terminal of the potentiometer to the end of the bar and clipping the other terminal in turn to the same element of successive thermocouples. The potential distribution will be somewhat as shown by the heavy line of Fig. 62*C*. On account of the increased temperature at the center, the resistivity and hence the potential fall per centimeter will be greater than at the ends. From this curve the slope $\partial V/\partial x$ may be observed at the various temperatures, and hence the Wiedemann-Franz constant evaluated.

Table 8 shows the values of κ, together with $1/\sigma$ and $\kappa/\sigma T$ for copper, at various temperatures. These data, shown graphically in Fig. 63, reveal the inadequacy of the Wiedemann-Franz law at low temperatures.

The suggestion was made by Koenigsberger[14] that the observed thermal conductivity is the combination of two effects. One of these factors is the electron conductivity, and superimposed upon this is the transmission of an atomic disturbance having somewhat the nature of an acoustical wave. This idea has recently been more fully elaborated by Grüneisen and Goens,[15] who have studied the effects of different amounts of impurities in certain metals upon electrical and thermal conductivities. They assumed that the addition of impurities would affect the electrical conductivity and that part of the thermal conductivity due to the electrons, but would not affect the other type of thermal conductivity. Then by extrapolation the individual effects could be analyzed.

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[14] J. Koenigsberger, *Phys. Zeit.*, **8**, 237 (1907).

[15] E. Grüneisen and E. Goens, *Zeit. Phys.*, **44**, 615 (1927).

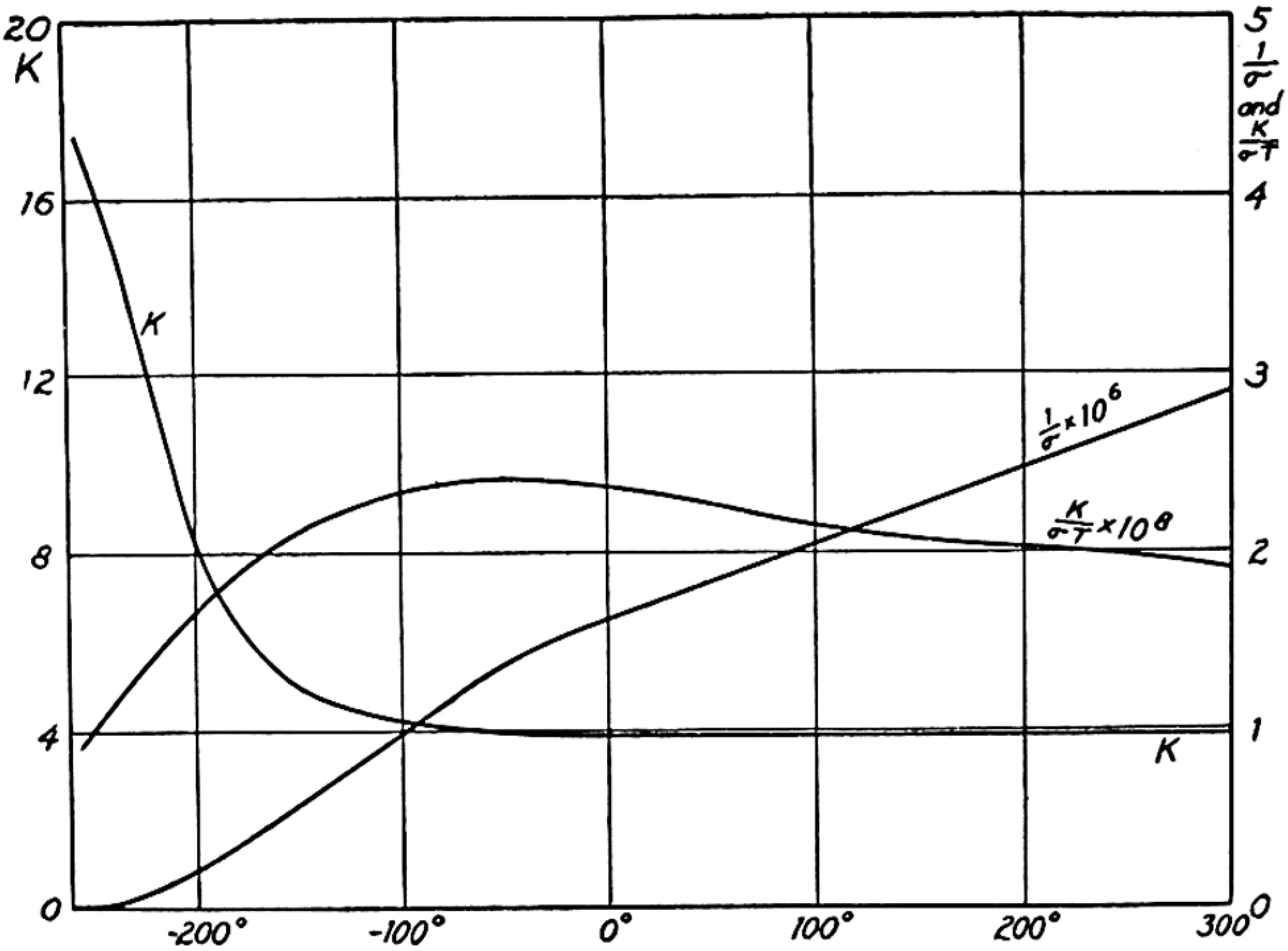

FIG. 63. Thermal and electrical conductivities and their ratio for copper at various temperatures.

TABLE 8

VARIATION OF THERMAL CONDUCTIVITY (κ), ELECTRICAL RESISTIVITY ($1/\sigma$) AND $\kappa/\sigma T$ FOR COPPER WITH TEMPERATURE

Temperature, deg. C.	Thermal Conductivity, Joules cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$	Electrical Resistivity, Ohm cm. $\times 10^6$	$\frac{\kappa}{\sigma T} \times 10^8$
−252.6	17.45	0.011	0.91
−240	15.25	0.021	1.01
−200	8.16	0.201	2.26
−160	4.55	0.492	1.98
−100	4.13	0.960	2.29
−50	3.94	1.44	2.54
0	3.93	1.64	2.38
+50	3.92	1.84	2.27
100	3.90	2.05	3.15
150	3.89	2.25	2.07
200	3.87	2.47	2.02
250	3.85	2.68	1.98
300	3.80	2.90	1.90

On the basis of the classical theory the existence of these free conduction electrons would have raised other difficulties. They should have offered a substantial contribution to the specific heat of the substance so that the molecular heat of electric conductors might have been expected to be much greater than that of nonconductors. This is not true, however. This negative result is predicted in the more recent theory of Sommerfeld.

Conductivity of Aeolotropic Substances. Many substances, although homogeneous throughout, exhibit different values of thermal conductivity according as this quantity is measured in different directions in the specimen. Such substances are called aeolotropic. Thus wood was observed by Tyndall[16] and Knoblauch[17] to be a much better conductor of heat in a direction parallel to the grain than at right angles to the grain. Likewise[18] laminated rocks such as mica have greater conductivities in a direction parallel to a cleavage surface. This aeolotropism would of course be expected in large single crystals which show crystallographic asymmetry in the three directions. H. de Senarmont[19] was perhaps the first to study this effect in single crystals. Further studies to determine the absolute value of the thermal conductivity in any direction have been carried out by Lodge[20] and Lees.[21]

Fluids and Convection. The application of heat to any restricted portion of an expansible fluid will result in this region of the fluid having a decreased density. Hence, if there is any fluid of greater density above this region, natural convection currents of heated material will develop. This heated material may give up its heat in its new position to its surroundings by both radiation and conduction. Transfer of heat by this process is called convection. It is evident that in any attempt to determine the pure coefficient of thermal conductivity of a fluid, care must be observed to avoid effects due to convection. Thus, if arrangements be made so that heat is supplied at a top horizontal surface and abstracted from the bottom, then most of the experimental methods already described for solids are directly applicable to liquids. Many such experiments on various liquids have been performed. Representative of these is the experiment of Jakob on water, using a parallel plate method with heat supplied at the upper surface. The value of the thermal conductivity of liquids is usually very small; thus for water Jakob[22] found that for temperatures up to 80° C. the coefficient of thermal conductivity could be satisfactorily represented as follows:

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[16] J. Tyndall, *Phil. Mag.*, [4] **6**, 121 (1853).

[17] H. Knoblauch, *Pogg. Ann.*, **105**, 623 (1858).

[18] E. Jannettaz, *Soc. Geol. Bull.* (*Paris*), **1**, 117 (1873).

[19] H. de Senarmont, *Ann. Chim. Phys.*, [3] **21**, 457 (1847).

[20] O. Lodge, *Phil. Mag.*, **5**, 110 (1878).

[21] C. H. Lees, *Phil. Trans.*, **183**, 481 (1892).

[22] M. Jakob, *Ann. Physik*, **63**, 537 (1920).

$$\kappa = 0.001325(1 + 0.002984T) \tag{65}$$

where T is the temperature in degrees centigrade.

Conductivity of Gases. In the case of gases the problem of pure thermal conductivity is still further complicated and is in fact inseparable from the phenomenon of radiation. That gases are very poor conductors of heat is of course evidenced by the enormous decrease in the conductivity of solids when they are made porous in any way. One of the earliest experiments dealing with the conductivity of gases was that of Andrews[23] with an apparatus similar to that represented in Fig. 64. A thin platinum wire was stretched at the axis of a cylindrical gas-tight tube. With the tube evacuated the wire was heated with sufficient current to give it a dull red glow. At this temperature its color changes markedly with a slight change in temperature. In this condition various gases were introduced in turn into the cylindrical space. It was observed that for the introduction of all gases except hydrogen the wire glowed more brightly or became warmer. The first conclusion that one might draw from this observation is that hydrogen is a much better conductor of heat than other gases, and that other gases are poorer conductors than a vacuum. This, of course, cannot be true; a more rational explanation is that there are manifest here all three agencies of transmission — conduction, convection, and radiation. This last process is the sole factor which allows a certain transfer of heat when the tube is evacuated. When a gas is introduced in the cylindrical space a part of the radiant energy will be absorbed in the gas and hence not be entirely lost to the inner wire. Now if the absorption in hydrogen, as would be expected, is small, then there are present

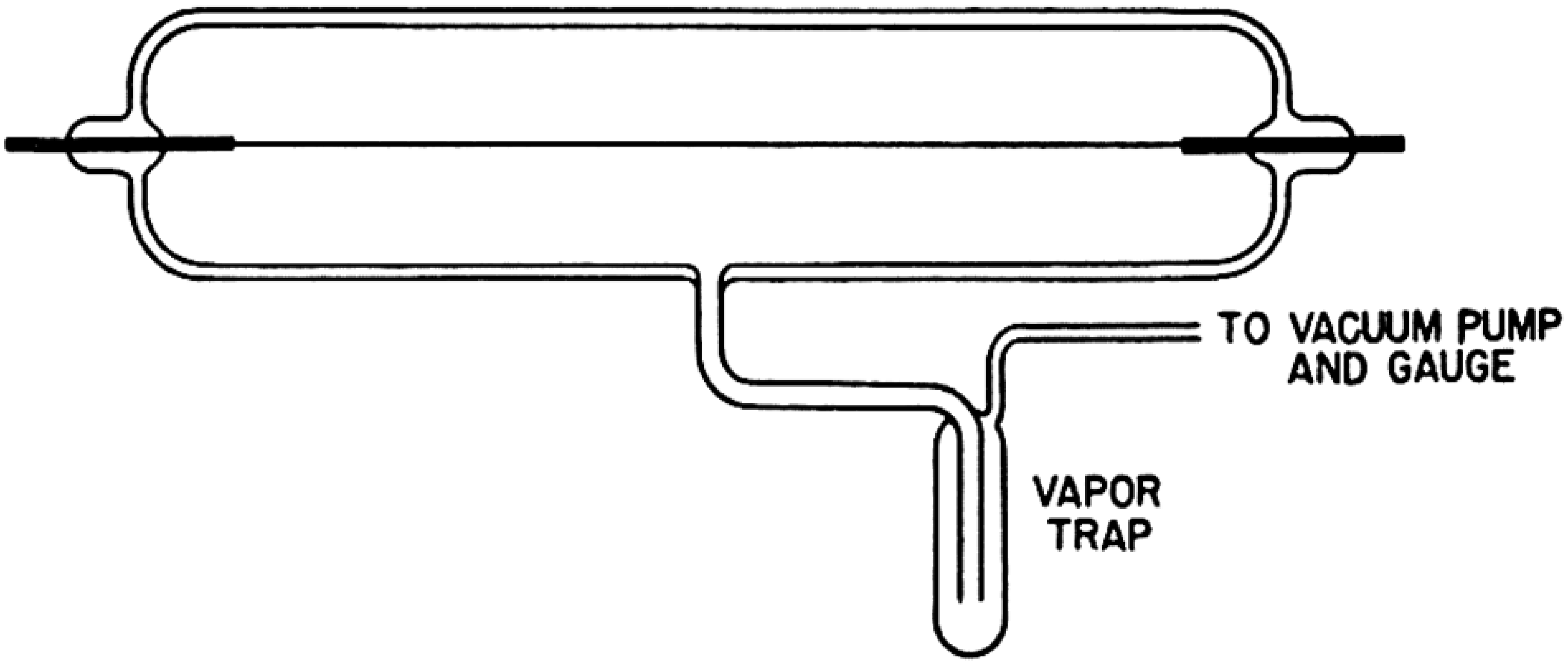

FIG. 64. Apparatus to study the transfer of heat by gases.

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[23] T. Andrews, *Proc. Roy. Irish Acad.*, **1**, 465 (1840).

convection, conduction, and almost full radiation, whereas for a heavy gas there would be conduction, convection, and greatly reduced radiation.

The method of Andrews has been employed in modified form in many other investigations.[24] In some of these the absolute thermal conductivity is obtained.

The values of Weber for the conductivities of various gases at a temperature of 0° C. in cal. deg.$^{-1}$ C. cm.$^{-1}$ sec.$^{-1}$ are collected in Table 9.

TABLE 9

THERMAL CONDUCTIVITIES OF VARIOUS GASES

Gas	$\kappa \times 10^4$
Hydrogen	4.165
Helium	3.438
Neon	1.089
Methane	0.720
Oxygen	0.576
Nitrogen	0.566
Air	0.568
Carbon dioxide	0.339

To compare the heat transfer at different pressures it is necessary that the temperature distribution be the same in each. This may be accomplished by connecting an ammeter in series with the filament shown in Fig. 64 and a voltmeter across the terminals so as to indicate the potential fall in the filament. The steady state at any particular pressure is quickly attained, and while the pressure is kept constant, several different currents I are made to pass through the filament and the corresponding values of the potentials E are observed. From the product EI the heat transfer is computed at the temperature indicated by the ratio E/I, which is a measure of the resistance of the filament.

This procedure is repeated at several different pressures and the data at each pressure plotted as shown in Fig. 65*a*. Now by noting the intercepts on these power curves at any chosen value of E/I, the heat transfer for identical temperature gradients but different pressures may be evaluated. These data may be represented graphically, yielding a curve as shown in Fig. 65*b*. It may be preferable to plot the logarithm of the pressure as abscissa.

The Pirani Pressure Gage. In low-pressure technique a very useful pressure gage, first attributed to Pirani,[25] makes use of this varying conductivity of a gas with a change in pressure. A tube similar to that shown in Fig. 64 is attached to the volume to be evacuated. The resistance of the filament forms one of the arms of a balanced Wheatstone bridge circuit. Any change in pressure causes a corresponding change in resistance, and thereby unbalances the bridge.

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[24] A. Schleiermacher, *Wied. Ann.*, **34**, 626 (1888); A. Eucken, *Phys. Zeit.*, **12**, 1101 (1911); S. Weber, *Ann. Physik*, **54**, 437 (1917); E. Schneider, *Ann. Physik*, **79**, 177 (1926).

[25] M. v. Pirani, *Verh. deut. phys. Ges.*, **8**, 686 (1906.)

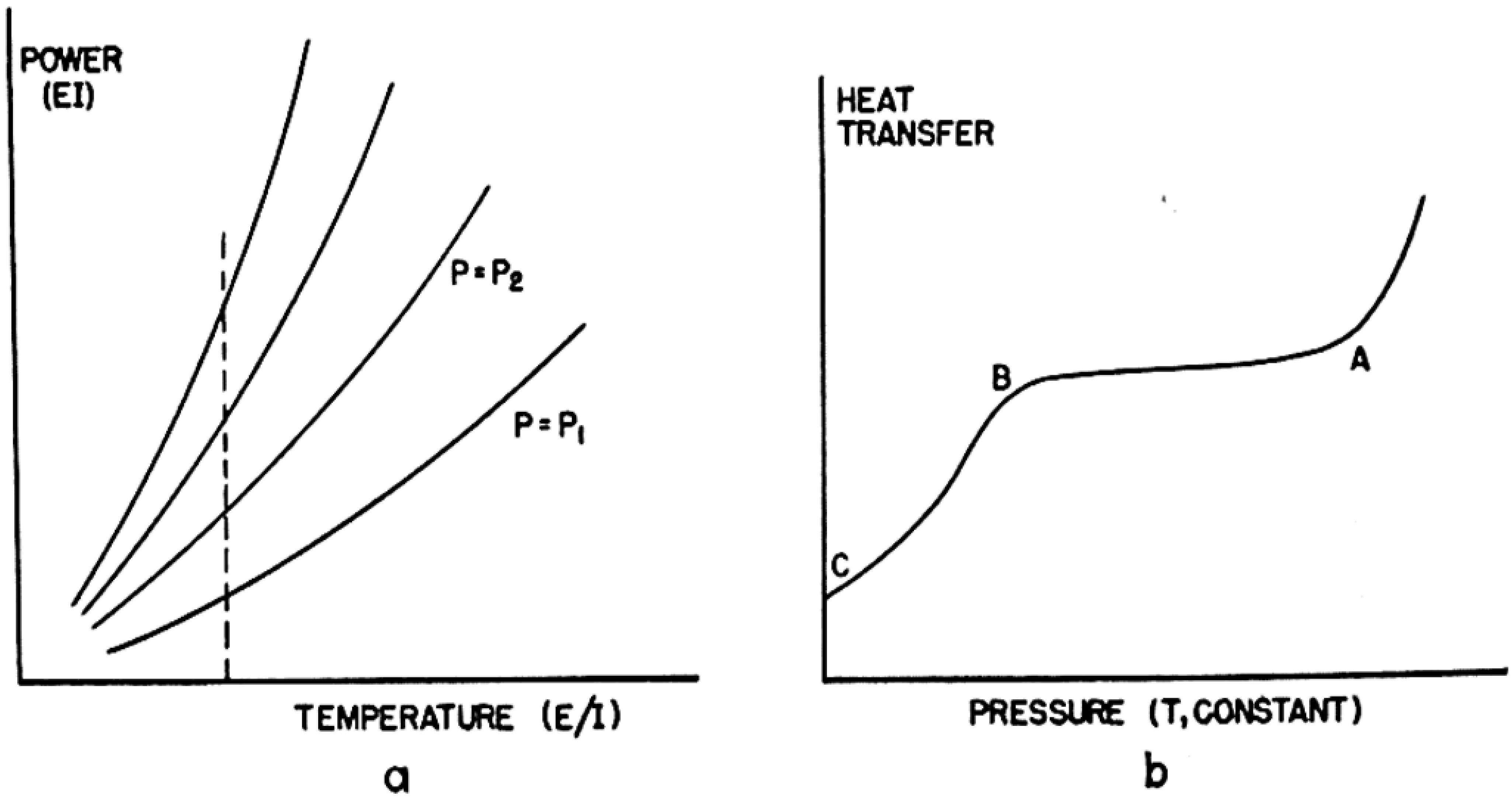

FIG. 65. Heat transfer through gases at (*a*) certain fixed pressures and various temperatures and (*b*) constant temperature difference and varying pressure.

Thermal Conductivity of Gases from Kinetic Theory. The conduction of heat in gases must be thought of as a directed transport of energy due to the random motion of the particles of the gas. Since there is no accumulation of gas in any part of the volume, the number of particles passing through any area per second must be the same in opposite directions. The net energy per second passing through unit area of an equitemperature surface is the difference between the total energies of all the particles arriving at one side and that of the equal number of particles coming to the same area from the opposite direction in the same time. The particles that come from the direction of higher temperature possess on the average a greater kinetic energy than those coming from the colder side. This energy flux was evaluated by Maxwell leading to an expression for the thermal conductivity. He predicted for air a value of 0.000052 calories per cm.^{2} per second for a gradient of 1° C. per cm. This estimate was found to be in good agreement with the observed value of 0.000056 in the same units.

He further reasoned that the thermal conductivity of a gas should be independent of the pressure, a result found to agree with experimental observation when convection is avoided, except at very low pressures. This behavior is shown in Fig. 65*b*, for the part of the curve between *A* and *B*. In this range of pressure the mean free path of the particles is small compared with the thickness of the transmitting layer of gas. On increasing the pressure the number of carriers is increased but this is offset by the decrease in the mean free path. For pressures greater than A, convection of the gas exists and accounts for the additional heat transfer. At pressures below B, the mean free path is greater than the thickness of the conducting layer, and hence a decrease in the number of carriers results in a decreased transmission. The ordinate C at zero pressure in Fig. 65*b* indicates the heat transfer by radiation alone.

Maxwell developed an expression relating the thermal conductivity κ, the specific heat under constant volume $(\text{S.H.})_v$, and the coefficient of viscosity η of a gas. This coefficient η (see page 51) is defined as the tangential force per unit area divided by the ratio of the velocity v of a parallel layer to the perpendicular distance d between the two surfaces, so that $\eta = Fd/Av$. The thermal conductivity was expressed as follows

$$\kappa = a(\text{S.H.})_v\eta \tag{66}$$

The constant a is calculable and was computed to be 2.5, when cgs. units are used for all quantities, except that heat is measured in calories. A portion of a table compiled[26] to show this relationship is presented in Table 10. It is apparent that the computed value of a agrees with the experimental value for monatomic gases such as helium and argon. For diatomic and polyatomic gases the constant a is smaller in value.

TABLE 10

RELATIONSHIP BETWEEN THE SPECIFIC HEAT, THE COEFFICIENT OF VISCOSITY AND THE THERMAL CONDUCTIVITY FOR A FEW GASES

Gas	$(\text{S.H.})_v$	$\eta \times 10^4$	$\kappa \times 10^4$	$a = \dfrac{\kappa}{(\text{S.H.})_v\eta}$
He	1.255/1.66	1.883	3.27	2.31
A	0.0744	2.108	0.385	2.47
H_2	2.406	0.852	3.63	1.76
O_2	0.153	1.925	0.535	1.79
CO_2	0.160	1.428	0.325	1.45
N_2O	0.220/1.317	1.364	0.334	1.47

Thermal Conductivity at Very Low Temperatures. At very low temperatures the thermal conductivity of many liquids and solids is found to vary anomalously. Those metals that become superconductors electrically at definite low temperatures may also exhibit abrupt changes in thermal conductivity. There is, however, no general rule to describe their behavior, thus on cooling indium through 3.37° K. an abrupt increase occurs in both the thermal and electrical conductivities, whereas on cooling lead through 7.26° K. the electrical conductivity increases and the thermal conductivity decreases.

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[26] E. O. Hercus and T. H. Laby, *Proc. Roy. Soc.*, **95**, 190 (1918).

For crystals that are not electrically conducting, the thermal resistance ω (i.e., $1/\kappa$) has been shown to decrease linearly with the absolute temperature to a minimum value at a temperature in the neighborhood of 10° K. On cooling below this temperature the resistance increases rapidly. The thermal conductivity of both normal and superconducting materials is affected by the application of magnetic fields. Liquid helium at 1.8° K. has been shown[27] to possess a thermal conductivity eight hundred times that of copper at ordinary temperatures.

QUESTIONS AND PROBLEMS

1. A room has 10 windows, each 1 meter square. The glass has a thickness of ¼ cm. How many grams (or pounds) of coal need be burned per day to maintain a temperature of 20° C. within, when the outdoor temperature is −10° C.? The heat of combustion of coal is approximately 7,000 cal. per gm. Explain your unreasonable answer.

2(*a*). Develop an equation applicable to the flow of heat in material in the form of a uniform spherical shell heated to a steady temperature within.

(*b*). Two concentric spheres of radii 5 cm. and 15 cm. have their annular cavity filled with a material whose conductivity is desired. It is found that when energy is supplied steadily at the center at a rate of 8 watts, a difference of temperature of 80° C. is maintained between the two spheres. Determine the thermal conductivity.

3. A wire whose resistance is 0.1 ohm per cm. lies at the geometric axis of a cylinder of cement and carries a current of 5 amp. The inside radius of the cylindrical shell of cement is 0.05 cm.; its outside radius is 1 cm. A difference in temperature of 125° C. exists between the inner and outer surfaces of the material. Express the thermal conductivity of the cement.

4. A long nickel bar is heated at one end. Where the temperature is 70° C. the variation in the temperature gradient is found to be 0.25° per cm. per cm. A separate test in which the bar was uniformly heated and allowed to cool showed a rate of cooling of 2.20° C. per minute at 70° C. Express the diffusivity of the material. Assuming the density to be 8.9 gm. per cm.^{3} and the specific heat 0.1 cal. per gm. per deg. C., what is the thermal conductivity?

5. In the method of periodic flow a rod is heated at one end with a heating cycle of 3.5 minutes. It is found that for a temperature maximum to travel from one stationary thermocouple to another, separated by a distance of 6.8 cm. along the rod, a time of 1.6 minutes is required. Express the wavelength and the velocity of propagation of the wave, assuming a density of 8.5 gm. per cm.^{3} and a specific heat

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[27] W. H. Keesom, A. P. Keesom, and B. F. Saris, *Physica*, **5**, 281 (1938).

of 0.11 cal. per gm. per deg. C. Calculate the thermal conductivity. What results would be different if the period of the heating cycle was made 35 minutes?

6. On the basis of the explanation of both electrical and thermal conductivities by the assumption of free electrons, justify the Wiedemann-Franz law.

7. A bare copper conductor 1 cm. in diameter carries a current of 1,000 amps. Neglecting any change in resistivity with temperature, how much warmer is the wire at its axis than at the surface? Tell what determines the surface temperature.

CHAPTER V

RADIATION

Nature of Thermal Radiation. The heat resident in a body may be communicated to neighboring bodies even though no material substance connects them. This energy in transit is spoken of as radiant energy, and the process by which it is transferred is called radiation. Although the mechanism by which the emission and propagation takes place was not at first understood, evidence indicated quite definitely that the process followed precisely the same laws that applied to visible light. This conclusion was based upon many experiments dealing with the variation of intensity with distance, and the reflection and refraction of the heat rays.

Hence, the electromagnetic wave theory so successful in explaining optical experiments must be regarded as applying equally well to so-called " heat rays." In fact, we may generalize to the extent of calling all electromagnetic waves, heat waves, because if absorbed in matter they ultimately appear as heat. The only difference in the apparently distinct types of radiation is that of the wavelength or of the frequency of the waves. The following table shows the approximate wavelength limits for the various types of radiation.

Gamma rays	0.000?	$\rightarrow$ 0.150	$\times 10^{-8}$	cm.
X rays	0.1	$\rightarrow$ 150	$\times 10^{-8}$	cm.
Ultraviolet	100	$\rightarrow$ 3500	$\times 10^{-8}$	cm.
Visible	3500	$\rightarrow$ 7800	$\times 10^{-8}$	cm.
Infrared (heat)	0.000078	$\rightarrow$ 0.04		cm.
Radio	0.04 cm.	$\rightarrow$ 10	$\times 10^{6}$	cm.

Since the radiation from ordinary hot furnaces exhibits maximum energy in the infrared spectral region, this particular portion of the whole spectral scale is often called in a narrow sense " heat radiation." Thus one sees from Fig. 16 that a body at 1,000° K. radiates maximum energy in the spectral region of 3μ (30,000 Å).

Definitions. Without adopting any hypothesis regarding the mechanism of the emission or the absorption of radiation, it is possible to set up certain definitions of quantities involved in the process. There is unfortunately considerable confusion in the meanings to be attached to certain of these terms.

(*a*) *A Black Body.* A surface is said to be black if it absorbs completely any radiation that is incident upon it. Theoretically a perfectly black surface does not exist, although there are many surfaces, such as a coating of lampblack, which reflect only an insignificant portion of any incident radiation. If a small aperture be made in the side of a hollow enclosure, then the chances that any radiation which enters the opening will ever get out again may be made vanishingly small by reducing the relative size of the aperture. This then constitutes a very close approximation to an ideal black body. When the enclosure is maintained at a constant temperature T, radiation of a definite amount per second will pass out through the aperture. This radiation is known as "black-body" radiation, and it has a characteristic distribution of energy with respect to wavelength and the temperature of the enclosure which is of great theoretical importance.

M. R

(*b*) *Total Surface Absorptivity.* This quantity denotes the fractional part of the total radiation incident upon a surface that is absorbed. It is denoted by A and is a pure fraction, having values ranging from zero up to unity — or 100 per cent. The particular value unity or 100 per cent is the case for a black body. This term (A) has very often been spoken of as "absorptive power." The use of a name involving "power" is objected to on the ground that the quantity in no sense possesses the dimensions of power, i.e., time rate of doing work. Total surface absorptivity is further not to be confused with "absorption coefficient." This latter term has to do with the rate of absorption of radiation in passing through an absorbing layer. Thus the emergent beam of radiation I is related to the incident beam I_0 as

$$I = I_0 e^{-\mu d} \tag{1}$$

where d is the thickness of the layer, μ is the linear coefficient of absorption of the material, and e is the base of the Naperian system of logarithms.

(*c*) *Monochromatic Surface Absorptivity.* This quantity is represented by the symbol A_λ and denotes the fractional part of the incident radiation in the particular wavelength band λ to $\lambda + d\lambda$, that is absorbed.

(*d*) *Total Surface Reflectivity.* This quantity is denoted by the symbol R. It represents the fractional part of the radiation of all wavelengths which when incident upon a boundary surface between two media is sent back into the medium from which it came. It is therefore a dimensionless quantity and should not be referred to as "reflective power." This quantity also depends somewhat upon the nature of the incident radiation. Since the radiation that is not reflected must be absorbed

$$R = 1 - A \tag{2}$$

(*e*) *Monochromatic Surface Reflectivity.* This quantity represents the fractional part of the incident radiation having wavelengths between λ and $\lambda + d\lambda$ which is not absorbed by the surface. It is denoted by R_λ, so that

$$R_\lambda = 1 - A_\lambda \tag{3}$$

(*f*) *Total Emissive Power.* The total energy radiated from a surface per unit of area per second without regard to wavelength or the direction of radiation is termed the total emissive power of the surface. This quantity may be expressed in ergs per square centimeter per second. Its magnitude depends upon the quality and the temperature of the surface. It is represented by the symbol e. Although, for convenience, the radiation is treated as coming from the surface, it must be recognized that it has its origin in the volume elements of the radiating body.

(*g*) *Characteristic or Monochromatic Emissive Power.* This quantity, represented by e_λ, is so defined that $e_\lambda d\lambda$ represents the radiated energy per square centimeter per second having wavelengths between λ and $\lambda + d\lambda$. Evidently then:

$$e = \int_0^\infty e_\lambda \cdot d\lambda \tag{4}$$

(*h*) *Total Emissivity.* The ratio between the emissive power of a surface and the emissive power of a black surface under identical conditions is called the emissivity of the surface. This is a pure number and may range in value from zero up to one, but it never exceeds unity. It is denoted by the symbol E and is sometimes called the "coefficient of emission."

(*i*) *Monochromatic Emissivity.* This quantity, represented by E_λ, is the ratio between the monochromatic emissive power of a surface and the characteristic emissive power of a black body under identical conditions.

(*j*) *Intensity of Emission from a Surface.* This concept is defined as the energy radiated per unit area per second per unit solid angle in a direction normal to the surface. This quantity represented by I obviously must be related by a constant to the emissive power of the surface. The relationship may be shown by reference to Fig. 66. A small radiating surface *ds* whose emissive power is *e* will radiate per second an amount of energy *eds*. The energy will pass out through an encircling hemisphere constructed about *ds* with the radius *r*. This same energy may also be expressed in terms of *I*. By taking as an element of surface a ring of width $r d\theta$ at an angle θ with the normal, an element of area $2\pi r \cdot \sin\,\theta \cdot r d\theta$ is obtained. This element of area subtends at the center a solid angle of $2\pi \sin\theta \cdot d\theta$. The component of area in the radiating surface effective for sending radiation through this ring is $ds \cdot \cos\theta$. The total energy per second through the whole hemisphere is then

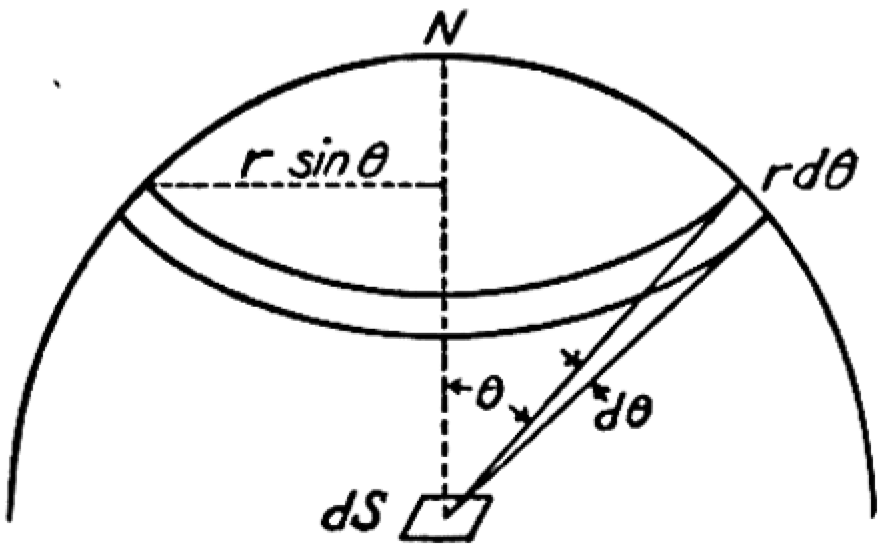

FIG. 66. The relationship between emissive power of a surface and the intensity of emission.

$$2\pi dsI \int_{\theta=0}^{\theta=\pi/2} \cos\theta \sin\theta d\theta = eds = 2\pi Ids \left[\frac{\sin^2\theta}{2}\right]_0^{\pi/2} = \pi Ids \qquad (5)$$

so that

$$e = \pi I \qquad (6)$$

(*k*) *The Monochromatic Intensity of Emission from a Source.* A quantity I_λ, called the monochromatic intensity of emission, is so defined that $I_\lambda\, d\lambda$ represents the energy radiated per second per unit area per unit solid angle in a direction normal to the surface, in the wavelength range λ to $\lambda + d\lambda$. A relationship corresponding to equation 6 may be written for the monochromatic quantities:

$$e_\lambda = \pi I_\lambda \qquad (7)$$

(*l*) *Intensity of Radiation.* The amount of radiant energy flowing through unit area per second is the intensity J of the radiation. For a plane electromagnetic wave in free space whose average magnetic vector is H and whose average electric vector is $\mathfrak{E}$, this flux of energy per second per square centimeter is given by the expression

$$J = \frac{C}{4\pi}[H\mathfrak{E}] \quad \text{(Poynting's theorem)} \qquad (8)$$

C is the velocity of light, and the bracket indicates that the vector product of $\mathfrak{E}$ and H is formed. Black-body radiation consists of a large number of wave trains simultaneously superimposed. Each wave train is associated with a definite quantum of energy and is called a photon.

The radiation from a surface of unit area in a definite direction has been found to vary with the cosine of the angle θ between the direction of emission and the normal to the surface. This relationship was discovered[1] by Lambert before 1760 and is known as Lambert's law. The product of the emitting area and the cosine of the angle θ gives the projected area normal to the direction of the radiation. Hence from any extended surface the intensity of radiation should be independent of the angle. In practice this is found to be approximately true for small angles but it does not hold for large angles. From a platinum surface the radiation has been found[2] to have a maximum greater than normal by 20 per cent, at an emergent angle of 80 degrees.

(*m*) *Monochromatic Intensity of Radiation.* This quantity, denoted by the symbol J_λ, is so defined that $J_\lambda \, d\lambda$ represents the flux in radiant energy, through unit area per unit time, having wavelengths between λ and $\lambda + d\lambda$.

Experiment of Leslie. One of the very first experiments dealing with the ability of various surfaces to radiate energy was carried out by Leslie[3] in 1804. In this investigation a hollow metal cube containing boiling water was mounted so that it could be rotated about a fourfold vertical axis. Each of the four vertical faces was coated with a different material to be studied. By rotation, any one of these four faces could be made to send its radiation to a receiving system consisting of a spherical mirror at the focus of which was the bulb of a gas thermometer. By using the rise in temperature of the bulb as an indicator of the emissivity of the surface, and assuming the emissivity of a surface of lampblack to be 100 per cent, Leslie gave values to the emissivity of various surfaces. A few of these are given as follows:

Lampblack	100%
Tarnished lead	45
Clean lead	19
Polished iron	15
Polished copper	18

These values for polished surfaces have been found to be too large, and the value for a particular substance may vary greatly with the temperature. It was very evident, however, that those surfaces which were good reflectors were themselves poor radiators.

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[1] J. H. Lambert (1728–77), *Photometria*, 1760.

[2] R. E. Stephens, *Jour. Opt. Soc. America*, **29**, 158 (1939).

[3] Sir John Leslie, *An Experimental Inquiry into the Nature and Propagation of Heat*, 1804.

A much more precise experiment relating the emissive power of a surface and its absorptivity was carried out by Ritchie[4] in 1833. From this investigation the conclusion could be drawn that, at a given temperature, the ratio of the emissive power of a surface to its absorptivity is a constant and the same for all surfaces.

This conclusion was not formally so stated until about 1860 when the subject was treated by Kirchhoff.

Kirchhoff's Law. This principle, that for the same wavelength and at the same temperature the emissive powers of all surfaces divided by their respective absorptivities yield the same constant, is known as Kirchhoff's[5] law.

This result may be demonstrated if one will consider a small body whose surface has an appreciable reflectivity, completely enclosed within a cavity all at a constant temperature T. Now if the enclosure is provided with a small opening, then through this aperture will stream per second per square centimeter a quantity of energy given by the emissive power of a black body at that temperature e_{BB}. This arrangement is shown in Fig. 67. Since there can be no continued accumulation of energy in any part of the enclosure it must follow that in the steady state the same quantity of energy per unit area per second must stream in opposite directions through any surface, however it be placed within the enclosure. That is, the intensity of radiation J within the enclosure is equal to the emissive power of a black body:

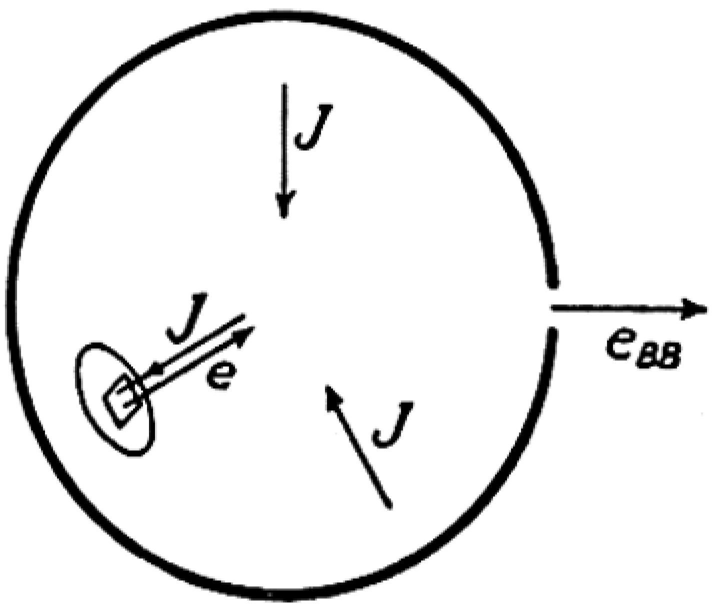

FIG. 67. A non-black body within a uniformly heated enclosure.

$$J = e_{BB} \tag{9}$$

For any element dS of the surface of the enclosed body, for the steady state, the energy radiated must just equal that received. The quantity radiated per second is edS, and that received on the same surface in the same time is $J \cdot A \cdot dS$, where A is the absorptivity of the surface, so that

$$edS = JAdS \tag{10}$$

or

$$\frac{e}{A} = J = e_{BB} \tag{11}$$

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[4] W. Ritchie, *Pogg. Ann.*, **28**, 378 (1833).

[5] G. Kirchhoff, *Pogg. Ann.*, **109**, 292 (1860).

That is, the ratio of the emissive power of a surface to its absorptivity is equal to the emissive power of a black body at the same temperature.

For a particular wavelength λ a similar monochromatic relationship must hold, for which

$$\frac{e_\lambda}{A_\lambda} = J_\lambda = (e_\lambda)_{BB} \tag{12}$$

Thus in an enclosure any body behaves as a black body. A non-black body will emit copiously radiation of the same wavelength that it absorbs most readily. A substance such as blue glass which appears blue by transmitted light, since the red is mostly absorbed, will, when heated, not in an enclosure, emit brilliant red light.

A plate of tourmaline when cold and exposed to unpolarized light transmits only a plane polarized beam and thereby reduces the total intensity of the light to one-half that of its incident value. If heated, this plate will emit light which is polarized in a plane at right angles to the beam that was transmitted when the tourmaline was cold.

The Pressure of Radiation. It was shown in equation 6 in Chapter II that an enclosed gas will communicate a pressure to the confining walls. If the velocities of the particles of the gas are distributed at random and if the impacts with the walls are perfectly elastic, it was shown that the average pressure P is equal to two-thirds of the energy contained in a unit volume of the gas in the form of kinetic energy of the particles.

In 1871, Maxwell[6] showed in a somewhat similar way that radiation within an enclosure might be expected to exert a pressure upon the containing walls. Maxwell's development was carried out by applying the electromagnetic theory to the radiation. The value of the average pressure to be expected upon a surface which absorbs completely all radiation incident upon it was shown to be

$$P = \tfrac{1}{3}u \tag{13}$$

Here u is the radiant energy of all wavelengths in a unit volume. The velocity of the radiation is assumed to be distributed at random with respect to direction.

This same result may be shown in a somewhat simpler manner from the point of view of the quantum theory. On page 179, it is shown that radiant energy in motion possesses momentum. The value of this momentum ϕ to be associated with any energy E is found by multiplying the mass m associated with this energy ($m = E/C^2$) by the velocity of the radiation C so that

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[6] J. C. Maxwell, *Electricity and Magnetism*, First Edition, Oxford, p. 391, 1873.

$$\phi = \frac{E}{C} \tag{14}$$

From the quantum idea the radiation incident upon any surface may be regarded as a collection of wave trains or photons. Each of these is characterized by a definite frequency ν, an energy $h\nu$, and a momentum $h\nu/C$, where h is the Planck constant. The total momentum received per second per square centimeter is then the sum of the normal components of $h\nu/C$, and this by definition is equal to the pressure P which the surface experiences.

Now, if it be imagined that the direction of all radiation is normal, and toward the surface under observation, then the energy streaming into a unit of the surface in unit time is equal to the velocity of the radiation C times the amount of radiant energy in unit volume. That is,

$$\sum h\nu = Cu = mC^3 \tag{15}$$

where m is the effective mass of the radiation in a unit volume. In this special case, the pressure P is then

$$P = \sum \frac{h\nu}{C} = u = mC^2 \tag{16}$$

Actually, however, the radiation is diffuse and there is no preferred direction, so that in general

$$C^2 = C_x^2 + C_y^2 + C_z^2 \tag{17}$$

Now if the pressure is observed on a yz plane, it is only the x component of the velocity that is effective. Thus,

$$P_{yz} = mC_x^2 = \tfrac{1}{3}mC^2 = \tfrac{1}{3}u \tag{18}$$

For diffuse radiation the yz plane is perfectly general. The energy u in a unit volume is moving in part to the right and an equal amount to the left along the x direction, so that the pressure on any exposed absorbing surface is one-sixth of the density of energy. Since a condition of thermal equilibrium exists at the surface, an additional equal pressure must be experienced by the absorbing surface because of its own radiation. Hence the total pressure is again equal to $u/3$. If the surface is a perfect reflector, then the momentum that is communicated by a quantum of radiation whose frequency is ν becomes $2h\nu/C$ and the pressure on the surface is one-third of the energy density.

It was almost thirty years after this prediction was made by Maxwell that the existence of a pressure due to radiation was experimentally demonstrated.

Two independent investigations, both establishing the effect conclusively, were carried out in the year 1900. One of the investigations was by Lebedew[7] and the other by Nichols and Hull.[8] In both the pressure was computed from the angular displacement produced by the radiation upon the moving system of vanes in an extremely sensitive radiometer. A brief description of a radiometer is given on page 168. The pressure to be measured in these experiments was of the order of one ten thousandth of a dyne per square centimeter.

Stefan-Boltzmann Law. It was suggested by Stefan[9] in 1879 that the total radiation from a heated body was proportional to the fourth power of its absolute temperature. He was led to this conclusion by certain meager data obtained by Tyndall in examining the radiation from a heated platinum wire. Tyndall had measured the relative total emission from the wire at 1,200° C. and 525° C. and found a value of 11.7 for the ratio of the total emissivities. The quotient of the fourth power of these absolute temperatures gave 11.6.

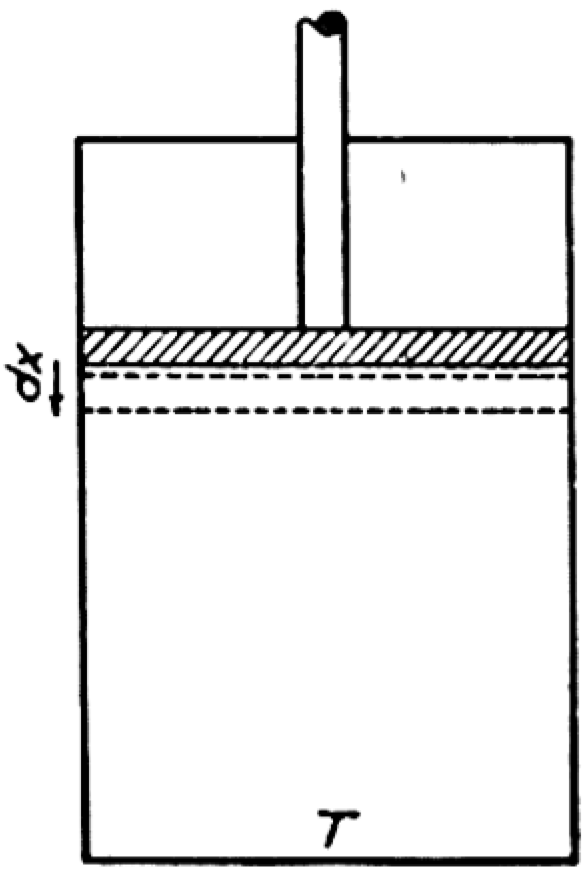

FIG. 68. Cylinder compressing radiation in Stefan-Boltzmann theory.

A few years later, Boltzmann[10] showed that the fourth-power law should be expected from general thermodynamic reasoning.

In this development, certain principles of thermodynamics elaborated more fully in Chapter VIII will be employed. A cylindrical evacuated cavity is imagined to be closed with a tight-fitting piston, the face of which, as well as the other interior walls, are assumed perfectly reflecting. Some small portion of the area such as the bottom is a black surface whose temperature is maintained at a constant value T from the outside as shown in Fig. 68. In the steady state the radiation in the enclosure will assume the distribution with respect to wavelength characteristic of black-body radiation, Fig. 16.

If now the piston is moved very slowly downward, the radiation will be compressed and the temperature of the enclosure slightly altered. At the same time a quantity of heat dQ may be transferred either into or out of the cylinder. The randomly directed radiation exerts a pressure P upon every exposed surface equal to one-third of the density of the radiant energy u. Hence in moving the piston downward so that the volume is reduced by an amount dV, work is done against this radiation pressure to the amount

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[7] P. Lebedew, *Ann. Physik*, **6**, 438 (1901).

[8] E. F. Nichols and G. F. Hull, *Phys. Rev.*, **13**, 293 (1901).

[9] J. Stefan, *Wien. Berichte*, **79**, 391 (1879).

[10] L. Boltzmann, *Wied. Ann.* **22**, 291 (1884).

$$PdV = \tfrac{1}{3}u \cdot dV \tag{19}$$

From the first law of thermodynamics the heat dQ[11] added or subtracted must balance the work done dW and the change in internal energy dU. Thus

$$dQ = dU + dW = d(uV) + PdV = d(uV) + \tfrac{1}{3}u \cdot dV \tag{20}$$

where U and u denote total energy and density of energy respectively. The cylinder containing the radiation has a certain entropy, and if the compression be regarded as a reversible process the total change in entropy is zero for the complete system. See equation 23, in Chapter VIII. For the loss or gain in entropy $(d\phi)$ of the cavity, due to the flow of heat dQ, it follows that

$$d\phi = \frac{dQ}{T} = \frac{d(uV)}{T} + \frac{udV}{3T} = V\frac{du}{T} + \frac{4}{3}\frac{udV}{T} \tag{21}$$

The change in entropy when expressed in terms of the changes in the temperature T and in the volume V is represented as an exact differential. Thus

$$d\phi = \frac{\partial\phi}{\partial T} \cdot dT + \frac{\partial\phi}{\partial V} \cdot dV \tag{22}$$

Equation 21 may be rewritten as

$$d\phi = \frac{V}{T}\frac{\partial u}{\partial T} \cdot dT + \frac{4}{3} \cdot \frac{u}{T} \cdot dV \tag{23}$$

so that

$$\frac{\partial^2\phi}{\partial T \cdot \partial V} = \frac{\partial\left(\frac{V}{T} \cdot \frac{\partial u}{\partial T}\right)}{\partial V} = \frac{\partial\left(\frac{4}{3}\frac{u}{T}\right)}{\partial T} \tag{24}$$

Performing the differentiation in equation 24 gives

$$\frac{1}{T}\frac{\partial u}{\partial T} = \frac{4}{3} \cdot \frac{1}{T} \cdot \frac{\partial u}{\partial T} - \frac{4}{3}\frac{u}{T^2} \tag{25}$$

---

[11] The quantities dQ and dW, unlike dU, are not exact differentials and could well be represented by some distinguishing symbol, but mathematically no distinction is necessary.

which becomes

$$\frac{\partial u}{\partial T} = \frac{4u}{T} \tag{26}$$

The integration of equation 26 leads to the relationship

$$u = aT^4 \tag{27}$$

Within the enclosure, the total density of radiation (u_{BB}) is related to the total intensity of radiation J_{BB} (i.e., energy of all wavelengths passing through unit area per second), and hence to the total emissive power e_{BB} of an imaginary opening in the enclosure. This relationship is

$$J_{BB} = e_{BB} = \tfrac{1}{4}C \cdot u_{BB} = \sigma T^4 \tag{28}$$

where C is the velocity of the radiation and σ is one of the fundamental constants of the universe. The constant $\frac{1}{4}$ may be shown by carrying out over a hemisphere an integration of the energy flow due to a streaming through unit area per second at the center.

This law which states that the density of radiation or the total emissive power of a black body is proportional to the fourth power of the absolute temperature of the body is known as the Stefan-Boltzmann law.

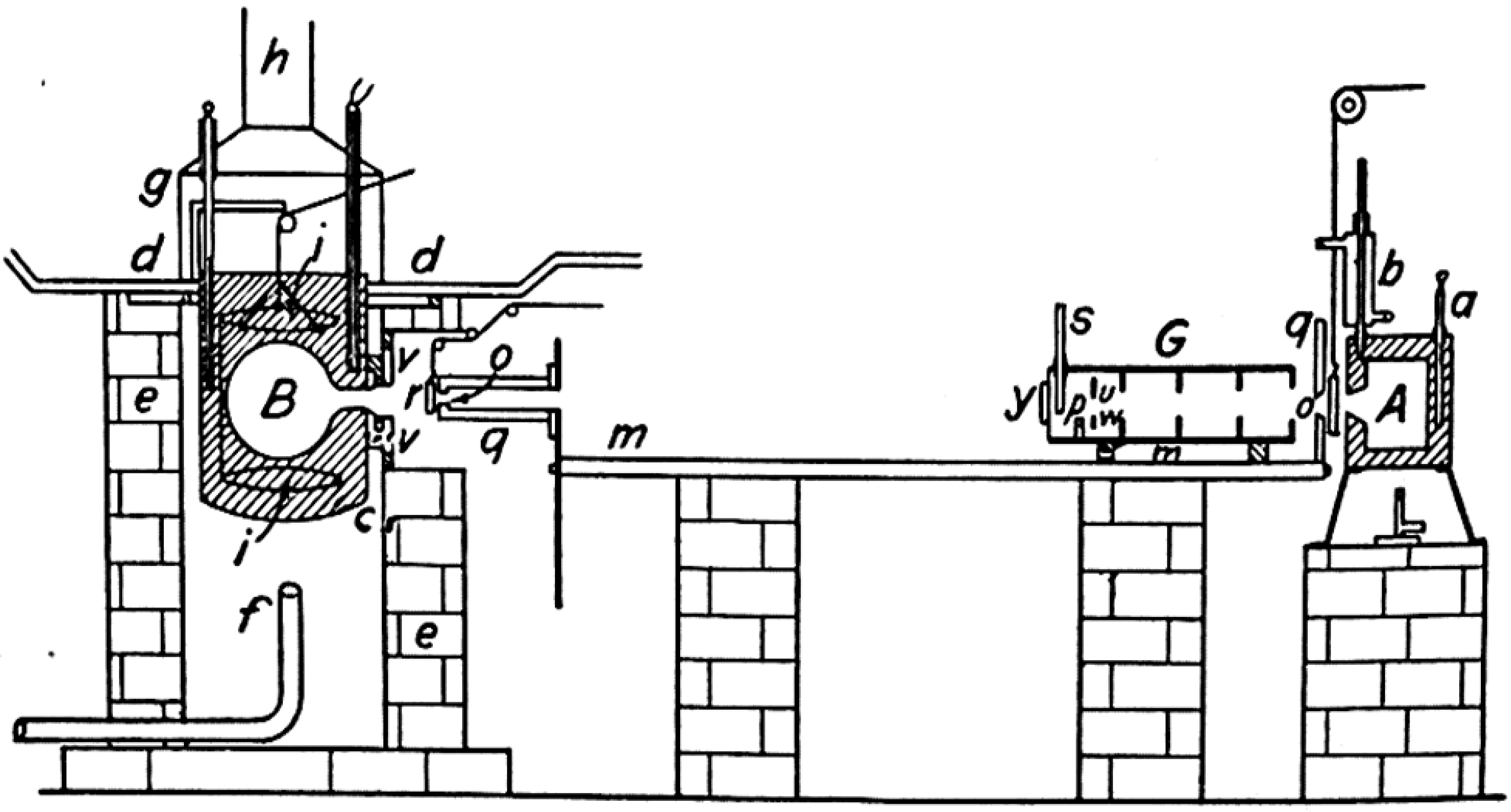

FIG. 69. Apparatus of Lummer and Pringsheim for studying total radiation.

Experimental Verification. The Stefan-Boltzmann law was verified experimentally by the careful experiments of Lummer and Pringsheim[12] for temperatures between 100° C. and 1,300 C. The apparatus employed in this investigation at the higher temperatures is shown in Fig. 69. The body B was a spherical shell of metal blackened inside and heated uniformly to a measured high temperature T. A was a standard blackened cavity heated always to the temperature of boiling water, and was used as a comparison source. G carried a bolometer and was adjustable in position between B and A. By alternately opening the shutters y and o and making use of the inverse square law, the intensities of radiation from B could be measured at various temperatures.

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[12] O. Lummer and E. Pringsheim, *Ann. Physik*, **63**, 395 (1897).

To evaluate the constant σ, characteristic of a black body, many experiments have been carried out. One of the first of these was due to Kurlbaum.[13] Later investigations have been reported by Féry,[14] Bauer and Moulin,[15] Valentiner,[16] Shakespear,[17] Gerlach,[18] and Westphal.[19] One of the more recent and perhaps most reliable investigations to determine σ was that of Coblenz.[20] In discussing the most likely value for σ, Coblenz adopts the value of 5.725×10^{-5} erg cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$. The later experiments of Hoffman[21] and Kussmann[22] gave values respectively of 5.764 and 5.795. The accuracy in this quantity is not great owing to the uncertainty in a correction applied for incomplete absorption in the receiving apparatus. As a final mean value Birge[23] recommends 5.672 ± 0.003 as the most probable value.

Laboratory Experiment on the Stefan-Boltzmann Constant. A rather simple arrangement may be employed to check the fourth-power law and to determine in an absolute manner the Stefan-Boltzmann constant. A satisfactory apparatus is shown in Fig. 70. A gas-tight chamber with a removable cover resting on a rubber gasket is evacuated to as low a pressure as practicable. Supported at the center of the evacuated space is a metal sphere, provided with an internal heating coil. A thin thermocouple in a shallow hole indicates the temperature of the sphere. The outer surface of the sphere is coated so as to approximate a perfectly black spherical radiator. The temperature T_0 of the outer jacket is kept at a known steady value by circulating water.

When electrical energy is supplied to the center at a steady rate P, the temperature T of the ball will come to an equilibrium value at which it is radiating energy at the same rate that it is receiving it. For this condition

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[13] F. Kurlbaum, *Ann. phys. Chem.*, [4] **65**, 746 (1898).

[14] C. Féry, *Compt. rend., Acad. Sci.* (Paris), **148**, 1043 (1909); **148**, 915 (1909).

[15] E. Bauer and M. Moulin, *Jour. Phys.*, **9**, 468 (1910).

[16] S. Valentiner, *Ann. Physik*, [2] **31**, 275 (1910).

[17] A. Shakespear, *Proc. Roy. Soc.* (*London*), **A**, **86**, 180 (1912).

[18] W. Gerlach, *Ann. Physik*, **38**, 1 (1912).

[19] W. H. Westphal, *Verh. deut. phys. Ges.*, **15**, 897 (1913).

[20] W. W. Coblenz, *Bur. Stand. Bull.*, **15**, 529 (1920).

[21] K. Hoffman, *Zeit. Phys.*, **14**, 301 (1923).

[22] A. Kussmann, *Zeit. Phys.*, **25**, 58 (1924).

[23] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

$$P = EI = 4\pi r^2\sigma(T^4 - T_0^4) \tag{29}$$

From which

$$\sigma = \frac{EI}{4\pi r^2(T^4 - T_0^4)} \tag{30}$$

The validity of the fourth-power law may be investigated by using several different input power rates, and observing the equilibrium temperature for each. From the Stefan-Boltzmann law it would be expected that

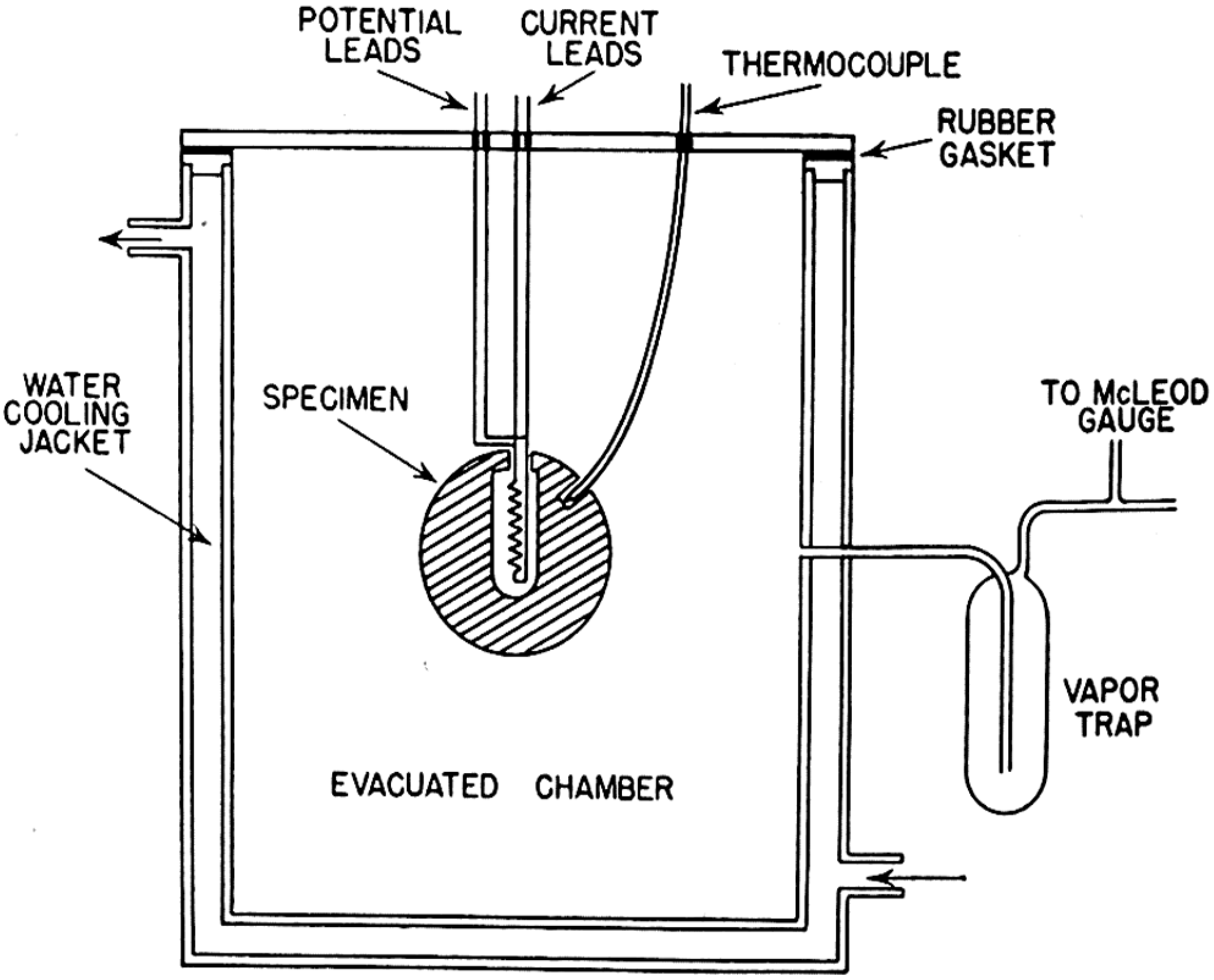

FIG. 70. Apparatus to determine the Stefan-Boltzmann constant.

$$\log P = \log R = 4 \log T + C \tag{31}$$

That is, if the logarithm of the input power is plotted against the logarithm of the equilibrium temperature on the absolute scale, a straight line of slope 4 should result.

This same equipment may be used to determine the specific heat of the material of the sphere. If when heated to a fairly high temperature the power input is reduced to zero, then the sphere will cool at a definite rate such that the loss by radiation per second is equivalent to the decrease in internal energy of the mass m of material, in the same time This may be expressed as

$$\frac{4}{3}\pi r^3\rho(\text{S.H.})\frac{dT}{dt} = 4\pi r^2\sigma(T^4 - T_0^4) \tag{32}$$

where ρ is the density of the material, (S.H.) is its specific heat, and dT/dt is the rate of cooling. From this equation the value of the specific heat may be obtained. Conversely, if the specific heat is known, then the cooling curve may be used to evaluate σ. In this event the internal heating coil is not necessary.

Newton's Law of Cooling. One of the earliest formulations regarding the rate of heat loss by a body to its cooler surroundings is attributed to Newton.[24] This statement, called Newton's law of cooling, asserts that the rate of cooling of a body under a definite set of conditions is proportional to the temperature difference between the body and its surroundings. Although this result clearly does not represent the truth when the difference in temperature between the body and its surroundings is large, still it is not badly in error for minute differences, and it is so simple in form that it has wide application.

That Newton's law is equivalent to the Stefan-Boltzmann law for small differences in temperature may be seen, if the higher temperature T of the radiating body be written as $(T_0 + \Delta T)$ where T_0 is the temperature of the surroundings. Thus by expansion, the expression of Stefan for the energy lost by radiation per sec., W becomes

$$\begin{aligned} W &= \sigma A(T^4 - T_0^4) = \sigma A[(T_0 + \Delta T)^4 - T_0^4] \\ &= \sigma A(4T_0^3\,\Delta T + 6T_0^2\,\overline{\Delta T^2} + \cdots) \end{aligned} \tag{33}$$

Neglecting higher powers of (ΔT) than the first, and grouping the constants together it follows that

$$W = C \cdot \Delta T \tag{34}$$

which is a formulation for Newton's law.

Wien's Law. The distribution of energy to be expected in the spectrum of the radiation from a black body was first discussed by Wien[25] in 1893. The procedure of Wien was somewhat like that of Boltzmann for the total radiation law. By assuming a cavity of perfectly reflecting walls, initially filled with black radiation and subjected to an adiabatic decrease in volume (dV), a certain change in the energy associated with any wavelength will take place. The energy initially resident in a certain wavelength region λ to $\lambda + d\lambda$ goes over into energy of shorter wavelengths, and its loss is made up by new energy coming into the initial spectral region. It was proved that, after the compression, the radiation remains as complete black-body radiation although the density of the energy and therefore the temperature are increased. The change in temperature may be found from Stefan's law involving the total density of energy and the temperature. This enabled Wien to determine the general distribution function for energy with wavelength at a given temperature.

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[24] Sir Isaac Newton, *Phil. Trans.*, **22**, 824 (1701).
[25] W. Wien, *Wied. Ann.*, **52**, 132 (1894).

For the adiabatic compression

$$dQ = 0 = d(uV) + PdV \tag{35}$$

where u denotes the density of energy of all wavelengths, V is the volume of the cavity, and P is the pressure of the radiation upon the walls. Equation 35 may be rewritten as

$$d(uV) = -PdV = -\tfrac{1}{3}udV = udV + Vdu \tag{36}$$

On integrating:

$$-\tfrac{4}{3}\log V = \log u \tag{37}$$

and

$$uV^{4/3} = \text{Constant } (c) \tag{38}$$

But u has been shown to be proportional to T^4; therefore:

$$TV^{1/3} = \text{Constant} \quad \text{or} \quad \frac{T}{T'} = \left(\frac{V'}{V}\right)^{1/3} \tag{39}$$

Equation 39 shows that a decrease in the volume V will alter the equivalent temperature of the radiation. In a similar way $T\,V^{\gamma-1}$ was found to apply to an adiabatically compressed gas.

Now from Doppler's principle any monochromatic beam suffering reflection on the contracting walls will leave the reflecting surface as of shorter wavelength or higher frequency.

The average change in wavelength $d\lambda$ suffered by an initially monochromatic beam of wavelength λ when the complete area as well as all possible incident angles are considered is shown to be very simply expressed[26] as

$$d\lambda = \frac{\lambda}{3V} \cdot dV \tag{40}$$

The integration of equation 40 shows that a wavelength λ goes over upon reflection into a shorter one λ' such that

$$\frac{\lambda}{\lambda'} = \left(\frac{V}{V'}\right)^{1/3} \tag{41}$$

Combining equation 41 with equation 39, it follows that

$$\lambda T = \lambda' T' \tag{42}$$

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[26] See M. Planck (translation by Masius), *Theory of Heat Radiation*, p. 79, 1914; Westphal, *Verh. deuts. phys. Ges.*, **16**, 93 (1914).

Equation 42 indicates that for any constituent part of the radiation, the product λT remains constant during the adiabatic change in volume, a result sometimes called the displacement law.

It must consequently follow for the distribution of energy at a temperature T', produced by a compression from T, that the energy in any wavelength λ' may be deduced from that of the wavelength λ at the temperature T by equation 42. In general, then, the density of radiation at any wavelength λ is dependent upon a function of λT which may be represented as $F(\lambda T)$. It must also be dependent upon some function of the temperature of the enclosure, which may be denoted as $F_1(T)$.

Hence the density of radiation for a particular spectral interval having wavelengths between λ and $\lambda + d\lambda$, represented by $u_\lambda \cdot d\lambda$, must be of the form

$$u_\lambda \, d\lambda = F_1(T)F(\lambda T)\, d\lambda = \frac{1}{T} F_1(T)F(\lambda T)\, d(T\lambda) \tag{43}$$

Now to satisfy the Stefan law the integral of this expression for the limits $T = 0$ and $T = \infty$ must yield a constant times T^4. It is apparent this will be the case if $F_1(T)$ involves T^5, since, in forming the definite integral, temperature will not appear. Hence the form of the expression for u_λ or equally well for the intensity of monochromatic radiation J_λ must be

$$J_\lambda = CT^5F(\lambda T) = C'\lambda^{-5}F(\lambda T) \tag{44}$$

where C and C' are constants.

To establish beyond this the form of $F(\lambda T)$ it becomes necessary to make an hypothesis regarding the mechanism of emission and absorption of radiant energy. By making certain assumptions regarding the equilibrium conditions between a gas and radiation, Wien[27] was able to express J_λ more directly. The first of these assumptions was that each gas particle sends out radiation whose wavelength is determined entirely by the velocity of the particle. Secondly, the intensity of the radiation emitted for a range in wavelength λ to $\lambda + d\lambda$ is proportional to the number of particles with velocities enabling them to radiate in this region. The intensity is also dependent upon a function of the velocity. The Maxwellian distribution function gives at once the numbers of particles having velocities between any limiting values v and $v + dv$ as $v^2e^{-(3v^2/2\bar{v}^2)}$ where v^{-2} is the mean square of the molecular velocities and is proportional to the temperature. From this, by comparison with equation 44, Wien was led to the better-known form of his equation

$$J_\lambda = C_1\lambda^{-5}e^{-(C_2/\lambda T)} \tag{45}$$

C_1 is a constant determined by the experimental arrangement; C_2 is a fundamental constant of nature. The ability of equation 45 to represent experimental results is discussed later.

Planck's Law. The first development of a distribution law by Planck[28] based upon classical principles resulted in an expression for J_λ identical with that of Wien. Convinced that this expression failed to represent completely the observed results, Planck carried out a development[29] based upon assumptions more radical. The primary assumption was that the interchange of energy between matter and radiation was not a continuous process, as had been assumed in the equipartition theory. Rather it was assumed that matter might be regarded as a collection of linear oscillators, and (according to his first development) when energy was emitted or absorbed it did so in multiples of some small energy unit. The energy unit was shown to be not a constant magnitude but to depend upon the frequency concerned. This unit of energy is often called the " quantum " and is denoted by ϵ. (In later developments, Planck also considered other suppositions, such as continuous absorption, and emission in quanta.)

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[27] W. Wien, *Ann. Physik*, **58**, 662 (1896).

[28] M. Planck, *Wied. Ann.*, **57**, 1 (1896).

The energy possessed by vibrators of a definite frequency must thus be zero or an integral multiple of ϵ. The oscillator physically may be regarded as the atom where low frequencies are involved, or the electron in the case of high frequencies.

From probability theory, if a certain amount of energy is to be distributed among a collection of N such oscillators so that some will possess 0ϵ, some 1ϵ, some 2ϵ, etc., then the number of oscillators possessing a certain integral number of quanta (n) is $N_0e^{-n\epsilon/kT}$, where k is the usual gas constant per molecule and N_0 is the number of oscillators possessing zero quanta. Hence the total number of particles N is

$$\begin{aligned} N &= N_0 + N_0e^{-\epsilon/kT} + N_0e^{-2\epsilon/kT} + \cdots + N_0e^{-n\epsilon/kT} \\ &= N_0(1 - e^{-\epsilon/kT})^{-1} \end{aligned} \tag{46}$$

For the total energy $\sum U$ of the N oscillators, it follows that

$$\begin{aligned} \sum U &= \epsilon N_0e^{-\epsilon/kT} + 2\epsilon N_0e^{-2\epsilon/kT} + \cdots + n\epsilon N_0e^{-n\epsilon/kT} \\ &= N_0\epsilon e^{-\epsilon/kT}(1 - e^{-\epsilon/kT})^{-2} = N\epsilon(e^{\epsilon/kT} - 1)^{-1} \end{aligned} \tag{47}$$

The average energy per oscillator $\overline{U}$ is $1/N$ of this value, so that

$$\overline{U} = \epsilon(e^{\epsilon/kT} - 1)^{-1} \tag{48}$$

Perhaps the most important step in the development followed. In this, ϵ is shown to be equal to $h\nu$, where ν is the frequency of the oscillator. By representing the motion of an oscillator on a momentum (P), displacement (q) coordinate system, an elliptical figure results. The areas of these ellipses as the energy takes values ϵ, 2ϵ, 3ϵ, etc., are ϵ/ν, $2\epsilon/\nu$, $3\epsilon/\nu$, etc. The various rings between any two successive ellipses all have a constant value denoted by Planck as a constant h. Thus

$$n\frac{\epsilon}{\nu} - (n-1)\frac{\epsilon}{\nu} = h \quad \text{or} \quad \epsilon = h\nu \tag{49}$$

Now from electromagnetic theory an oscillator of frequency ν in an enclosure will acquire an average energy $\overline{U}_\nu$ depending upon the density of the radiation $u_\nu d\nu$ of that particular frequency with which it is in equilibrium.

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[29] M. Planck, *Ann. Physik*, **4**, 553, *et seq.* (1901).

This relationship may be shown to be

$$\overline{U}_\nu = \frac{C^3}{8\pi\nu^2} \cdot u_\nu = h\nu(e^{h\nu/kT} - 1)^{-1} \tag{50}$$

but $u_\nu d\nu = -u_\lambda d\lambda$ and $\nu = C/\lambda$, so that

$$d\nu = -\frac{C}{\lambda^2} d\lambda \quad \text{and} \quad u_\nu = \frac{\lambda^2}{C} u_\lambda \tag{51}$$

By substitution in equation 50 the density of energy may be written as

$$u_\lambda = \frac{8\pi hC}{\lambda^5(e^{h\nu/kT} - 1)} \tag{52}$$

But as mentioned previously, in equation 28, the energy density of the radiation of a particular wavelength in the enclosure determines also the intensity of radiation for that wavelength in emission, that is,

$$e_\lambda = \frac{C}{4} \cdot u_\lambda \tag{53}$$

Hence it follows that

$$e_\lambda = J_\lambda = \frac{2\pi hC^2}{\lambda^5(e^{h\nu/kT} - 1)} = C_1\lambda^{-5}(e^{C_2/\lambda T} - 1)^{-1} \tag{54}$$

Equation 54 is the final form of the development due to Planck. The constants C_1 and C_2 have the same significance as in the expression of Wien, equation 45.

The Rayleigh-Jeans Law. A formulation to represent the distribution of energy in the radiation from a black body as a function of wavelength and temperature was proposed by Rayleigh[30] in 1900 and elaborated by Jeans[31] in 1909. In the original development of Rayleigh the intensity of radiation J_λ was expressed as

$$J_\lambda = \frac{C}{\lambda^4} \cdot T \cdot \frac{1}{e^{C_2/\lambda T}} \tag{55}$$

The exponential factor was introduced merely because of its success in the corresponding Wien expression. As a final result, Jeans expressed the quantity u_λ as follows:

$$u_\lambda = 8\pi kT\lambda^{-4} \tag{56}$$

where k is the Boltzmann gas constant. The Planck law degenerates to this expression for large values of λT. This may be shown by replacing e^x by $1 + x$ when x is very small.

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[30] Lord Rayleigh, *Phil. Mag.*, **49**, 539 (1900).

[31] Sir James Jeans, *Phil. Mag.*, **17**, 239 (1909).

At high temperatures it should thus follow that the radiation for long wavelengths is proportional to the absolute temperature. This is found to be approximately the case in practice. However, under other conditions, namely, short wavelengths and low temperatures, agreement between the observed experimental results and the predictions of the Jeans or Wien laws is entirely lacking.

Experimental Studies of the Spectral Distribution of Energy. One of the first precise experimental studies of the distribution of energy with wavelength, for the radiation from a black body, was carried out by Lummer and Pringsheim[32] in 1899. In this experiment the radiation from an electrically heated enclosure was refracted by a fluorite (CaF) prism. An arrangement of apparatus suitable for this investigation is shown in Fig. 71. The use of lenses to focus the radiation from the furnace F is of course prohibited by absorption effects, so that plane and spherical front surfaced mirrors M_1, M_2, M_3, M_4 are used to direct the radiation. A linear thermopile back of the slit at T serves to compare the intensities of radiation.

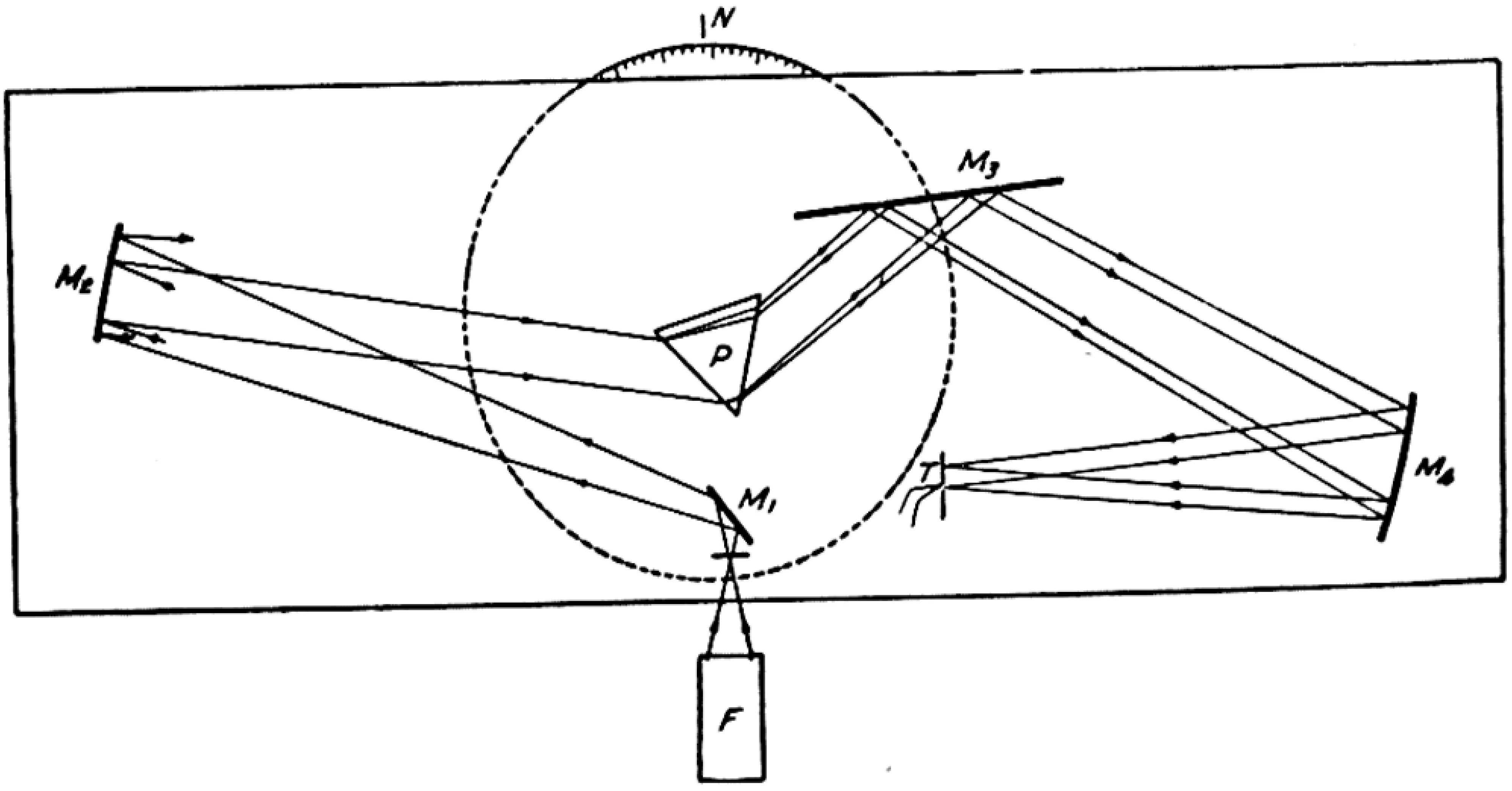

FIG. 71. A Wadsworth infrared spectrometer.

The apparatus shown is not that used by Lummer and Pringsheim but is that of a modern infrared spectrometer using an arrangement due to Wadsworth. The results of the investigation of Lummer and Pringsheim are shown in Fig. 16. These results appeared at first to be very well represented by the equation of Wien. A repetition of the experiment with greater precision, however, showed unquestionably a discrepancy between experimental and theoretical values for large values of λ or T (λT). This discrepancy served as the incentive for the epoch-making development of Planck. The equation of Planck was found to represent remarkably well the best experimental values then available. To test further this agreement, numerous painstaking researches have been made. The work of Rubens and Kurlbaum[33] for long waves and that of Paschen[34] for short wavelengths was reported as substantiating definitely the Planck law. The conclusions of Warburg[35] and Nernst,[36] who with their students, had made a systematic study of this problem, was that disagreements up to a few per cent still existed between observed and expected values. Coblenz,[37] however, in reviewing the field, concluded that experimental values were very satisfactorily represented by the Planck law. For C_2 he recommended a value 14,320 micron degrees. This conclusion is in agreement with the experiments of Rubens and Michel,[38] who reported that no discrepancy existed between experimental values and those to be expected from the Planck law for temperatures from −180° C. to 1,560° C. The distribution of energy with wavelength to be expected from the three different results is shown in Fig. 72 (Wien A, Planck B, and Rayleigh-Jeans C). This represents the radiation from a black body at 1,000° C.

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[32] O. Lummer and E. Pringsheim, *Verh. deut. phys. Ges.*, **1**, 215 (1899); *Ann. Physik*, **6**, 192 (1901).

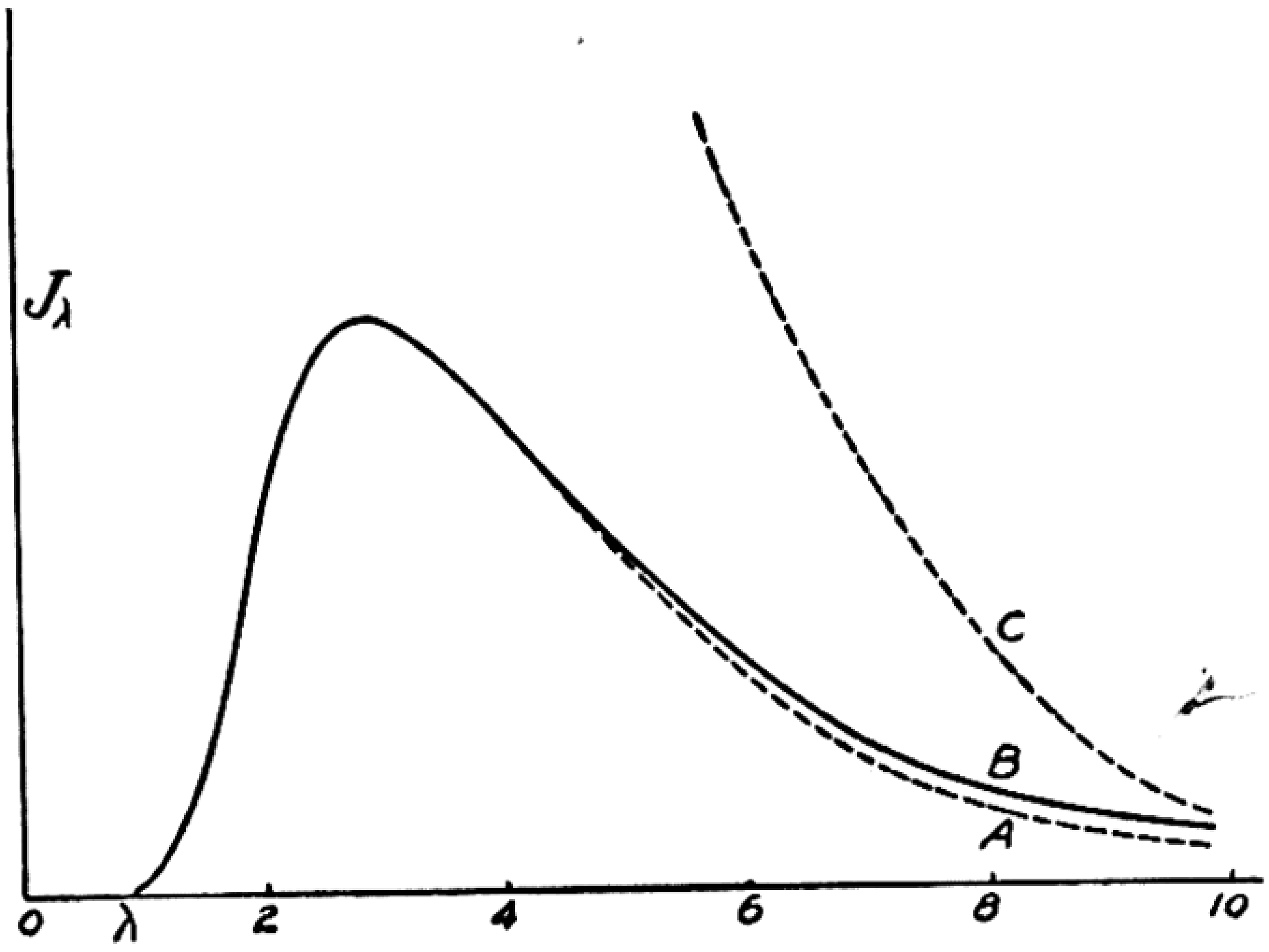

FIG. 72. The distribution of energy with wavelength: *A*. Wien law. *B*. Planck law. *C*. Rayleigh-Jeans law.

Corollaries of the Planck Law. *The Stefan-Boltzmann Relationship.* The Stefan-Boltzmann law follows directly from the Planck law by forming the areas under the distribution curves in Fig. 16. Thus the area A representing the energy of all wavelengths follows:

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[33] H. Rubens and F. Kurlbaum, *Ann. Physik*, **4**, 649 (1901).

[34] F. Paschen, *Ann. Physik*, **4**, 277 (1901).

[35] E. Warburg, *Ann. Physik*, **48**, 410 (1915).

[36] W. Nernst and T. Wulf, *Ber. deut. phys. Ges.*, **21**, 294 (1919).

[37] W. W. Coblenz, *Dict. Appl. Phys.*, Vol. IV, " Radiation."

[38] H. Rubens and G. Michel, *Verh. preus. Akad.*, **38**, 590 (1921).

$$A = e = \int_{\lambda=0}^{\lambda=\infty} J_\lambda d\lambda = C_1 \int_0^\infty \frac{d\lambda}{\lambda^5 (e^{C_2/\lambda T} - 1)} \tag{57}$$

Now applying the result of equation 51, the above integral by introducing x for $h\nu/kT$ becomes:

$$e \doteq C_1 \int_{\nu=\infty}^{\nu=0} - \frac{C}{\nu^2} \cdot \frac{\nu^5}{C^5} \cdot \frac{1}{e^x - 1} \cdot d\nu = C'T^4 \int_{x=0}^{x=\infty} \frac{x^3\, dx}{e^x(1 - e^{-x})}$$

$$= C'T^4 \int_0^\infty (e^{-x} + e^{-2x} + \cdots)\, x^3\, dx = C'T^4 \frac{\pi^4}{15} = \sigma T^4 \tag{58}$$

The constant C' has the value $(2\pi k^4)/(C^2 h^3)$, so that σ might be calculated from the other determined constants. Using for the gas constant per molecule k the value of Birge, 1.38047×10^{-16}; for h, the Planck constant 6.624×10^{-27}; and C the velocity of light 2.99776×10^{10}; σ is calculated to be 5.672×10^{-5}, a result considerably smaller than the experimental value of Coblenz.

The Displacement Law. By differentiating the Wien equation with respect to λ while keeping T constant and equating the result to zero (condition for maximum J_λ) it follows that

$$\frac{dJ_\lambda}{d\lambda} = -5C_1\lambda^{-6}e^{-C_2/\lambda T} + C_1\lambda^{-5}e^{-C_2/\lambda T} \cdot \frac{C_2}{\lambda^2 T} = 0 \tag{59}$$

Since C_1 and $e^{-C_2/\lambda T}$ cannot be zero, then it must follow that

$$5\lambda^{-6} = \frac{C_2\lambda^{-7}}{T} \tag{60}$$

or

$$T\lambda_{\text{max. energy}} = \frac{C_2}{5} = \frac{14{,}320}{5} = 2{,}864 \text{ micron degrees} \tag{61}$$

The value for this product found by Lummer and Pringsheim as best fitting their data was 2,940 micron degrees. The value 2,884 represents the averaged results of the most recent experiments[39] upon this quantity. The value of Birge[40] obtained by computation from other physical quantities is 2,897.1 micron degrees.

The ratio between the values of J_λ for the positions of maximum energy for two temperatures T_1 and T_2 is of considerable interest.

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[39] W. W. Coblenz, *Bur. Stand. Bull.*, **17**, 39 (1920).

[40] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

Equation 61 shows that, for the positions of maximum energy, λT must be a constant. Hence at these points $(e^{C_2/\lambda T} - 1)$ must be the same for the two curves. Then for the maxima of the two curves the intensities of radiation will have the ratio

$$\frac{(J_\lambda)_{T_1}}{(J_\lambda)_{T_2}} = \left(\frac{\lambda_{T_2}}{\lambda_{T_1}}\right)^5 = \frac{T_1^5}{T_2^5} \tag{62}$$

or

$$(J_\lambda)_{\text{max. energy}} = CT^5 \tag{63}$$

where C is a constant.

This relationship was found to fit well the observations of Lummer and Pringsheim.

Laboratory Experiment to Determine the Constant C_2 in the Wien Law. Assuming the equation of Wien to serve as the guiding law for optical pyrometers, a very simple experiment leads to the evaluation of the constant C_2. In extending the range of a pyrometer by the use of a sectored disk it was shown in equation 28, in Chapter I that if R denotes the ratio of the open to the total angular space on the disk then

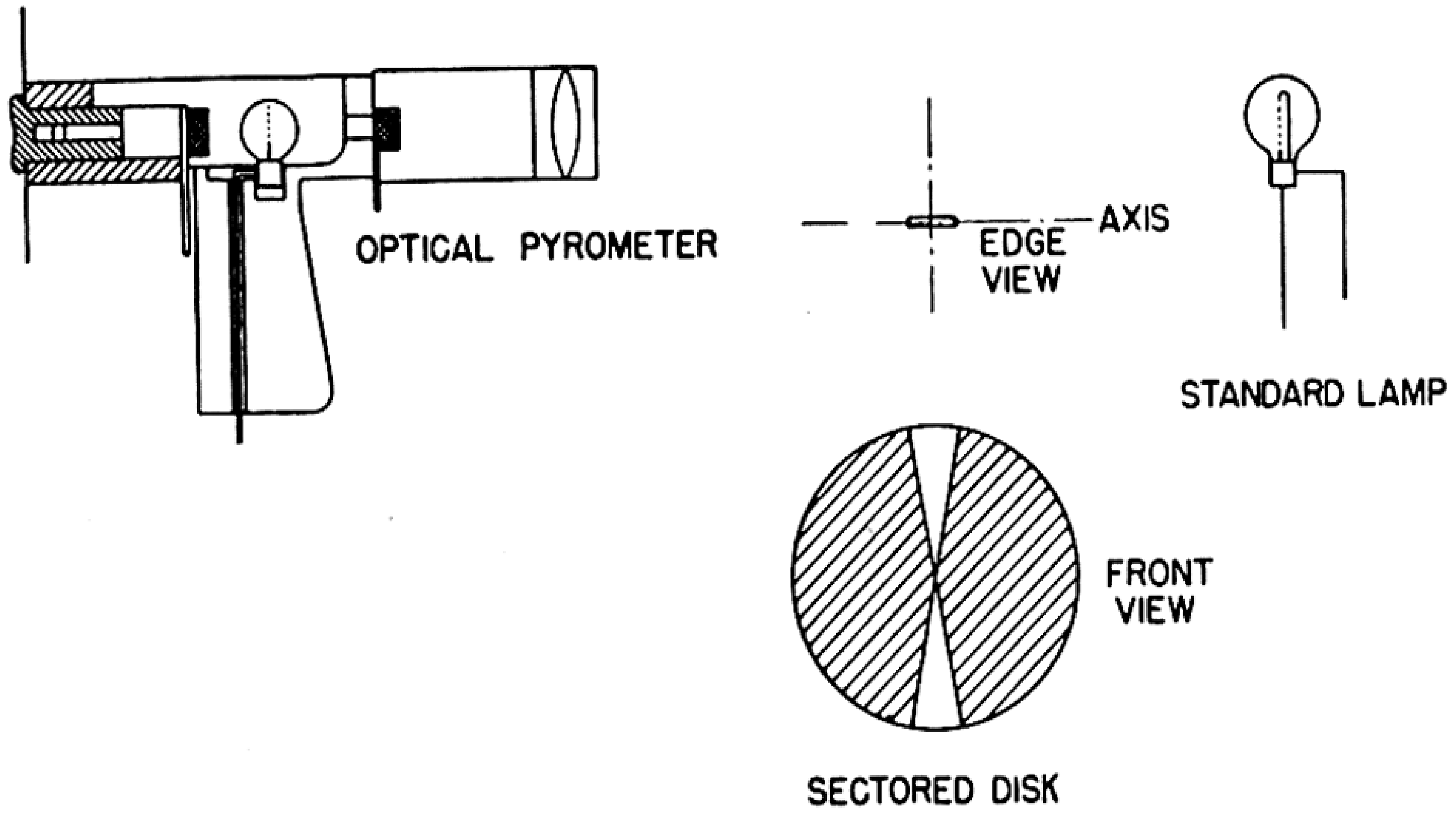

FIG. 73. Apparatus for the determination of the constant C in the Wien or Planck laws.

$$\frac{1}{T_{\text{true}}} - \frac{1}{T_{\text{app.}}} = \frac{\lambda}{C_2} \cdot \log_e R \tag{64}$$

Thus by sighting a pyrometer upon a source at a constant temperature, its true temperature T_{true} is given. Then by interposing a rotating sectored disk whose ratio of open to total space is R, an apparent temperature ($T_{\text{app.}}$) will be observed. The arrangement of this apparatus is shown in Fig. 73. Knowing the effective wavelength (λ) that is transmitted by the absorbing glass used, generally about 0.63 μ, and measuring the value of R, the only undetermined constant remaining is C_2. So that

$$C_2 = \frac{\lambda\, T_{\text{true}}\, T_{\text{app.}} \log_e 1/R}{T_{\text{true}} - T_{\text{app.}}} \tag{65}$$

The Solar Constant. One of the most important constants in the field of radiation is the solar radiation constant. This means the energy of all wavelengths normal to unit area per unit time in the sun's radiation at the earth's surface. It is, of course, a variable quantity with time, since the distance between the earth and the sun, and also the nature of the sun's surface which is exposed toward the earth, vary. Moreover, the measurement of the quantity is rendered difficult by the earth's atmosphere. In the infrared spectral region the atmosphere absorbs all radiation except a band between 8 and 15 microns in wavelength. In the early experiments the effect of the atmospheric absorption was accounted for by taking observations at successive intervals during the day and substituting the observed intensities into the general equation for absorption in which the variation in the thickness of the absorbing layer is known. Thus

$$J_1 = J_0 e^{-\mu t_1},\ J_2 = J_0 e^{-\mu t_2},\ \text{etc.} \tag{66}$$

The effective coefficient of absorption of the atmosphere is represented by μ, and the observed intensities for atmospheric path lengths t_1 and t_2 are J_1 and J_2, from which J_0 is found. The problem is, of course, complicated by the variation in atmospheric density as well as local atmospheric disturbances. The values obtained up to 1900 were considered in a report by Crova.[41] This included observations of Langley, Violle, Ångström, Crova, and others. The results of these various investigators, when expressed in calories per square centimeter per minute, ranged from one to four. The most recent determination, namely, that of Abbot and Fowle,[42] gives for the value of this constant when averaged for the years from 1905 to 1926 a mean value of 1.94 cal. per square centimeter per minute. Individual observations gave values ranging from 1.85 to 2.02. At a particular station, cycles of approximately two per month are commonly noticed.

The Radiometer. An interesting device capable of measuring the intensity of radiation, called the radiometer, was invented by Crookes.

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[41] A. Crova, *Ref. Cong. Int. de Phys.*, **3**, 453 (1900).

[42] C. G. Abbot, *Beiträge zur Geophysik*, **16**, 361 (1927).

This instrument has been modified by Rubens[43] and more recently by Nichols and Tear[44] so that it has a very great sensitivity. In its simplest form it consists of a very light system of two vanes of mica mounted at the ends of a horizontal support, the whole being suspended on a light quartz fiber, as shown in Fig. 74. This whole system is arranged in an evacuated space provided with a thin window for the entrance of radiation. One of the light mica vanes is a good reflector of radiation; the other is rendered a complete absorber by having its front face blackened. Now, when radiation is incident upon the system, the suspension may be actuated by a torque such that the blackened surface either comes toward or, vice versa, recedes in the direction of the radiation. The type of action which occurs is determined entirely by the pressure of the gas in the enclosure. If the enclosure is completely evacuated the polished surface will recede, since in front of it there will be a greater density of radiation, owing to reflection and hence a greater pressure of radiation upon its surface. On the other hand, if particles of gas remain in the enclosure they will rebound with a greater velocity from the warmer blackened surface and hence will communicate to it a greater momentum, causing it to recede. A small mirror (M) is carried on the horizontal support so that by reflecting a beam of light the angular deflection of the moving system may be observed.

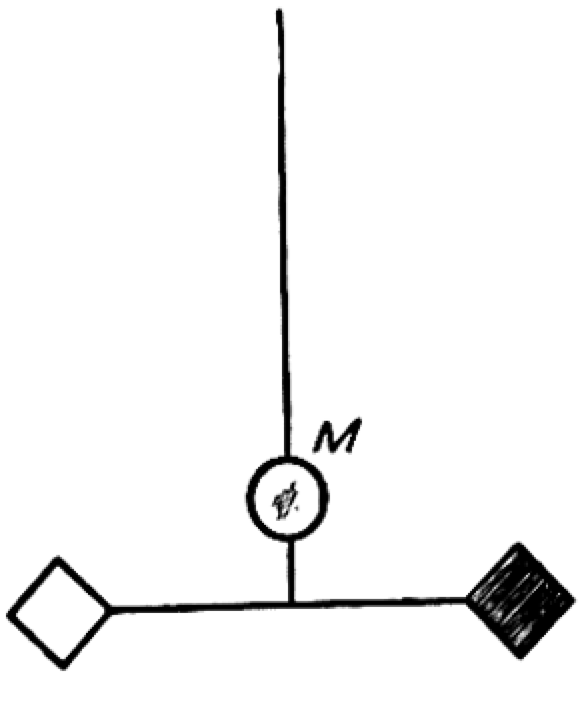

FIG. 74. Radiometer.

The Temperature of the Planets. The solar radiation constant at the earth is about 0.135 joules per cm.^{2} per sec. If this should be received by a small blackened conducting sphere, the temperature T of the sphere would attain an equilibrium value such that the radiation from the total surface is just equal to the energy received on the area of a great circle. Thus

$$\pi r^2 S = 4\pi r^2 \sigma (T^4 - T_0^4) \qquad (67)$$

where T_0 is the effective temperature of the surroundings. On inserting the value of σ and solving for T, the equilibrium temperature of 72° C. is obtained. If an equilibrium temperature is not attained on the sphere, either because of its large dimensions and poor conductivity or because of the absence of rotation, then the side radiated may be much warmer than the distant side. The condition on the planets is further complicated by the presence of atmospheres which scatter some of the incident radiation directly.

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[43] H. Rubens, *Zeit. Inst.*, **6**, 65 (1898).

[44] E. F. Nichols and J. D. Tear, *Astro. Phys. Jour.*, **61**, 17 (1925).

At Lowell Observatory a radiometer has been employed[45] in connection with the 40-in. reflector so that with the planet Mars the diameter of the planet's disk was as much as nine times the diameter of the receiving disk. To arrive at the temperature it was necessary to make observations with and without certain filters between source and receiver. Thus a water cell transmits well wavelengths between 0.3 to 1.4 microns. With this in place the scattered solar radiation would not be absorbed, but that radiation due to the emission of the low-temperature surface would be completely cut off. Other filters of quartz and fluorite were also used. A variation in temperature from −33° C. up to 7° C. was recorded, as different parts of the planet Mars were viewed. Some additional temperatures observed were: Uranus, −173° C.; Venus 57° C.; and the moon from 47° C. to 117° C.

QUESTIONS AND PROBLEMS

1. The solar constant at the earth's surface is 0.135 joules per cm.^{2} per sec. The radius of the sun is 430,000 miles, and the diameter of the earth's orbit is 186 million miles. Assuming the sun to be a black body, what is its temperature?

2. At what rate is the sun losing energy because of its radiation? Express in terms of kilowatts or horsepower.

3. Using the above value of the solar constant, what would be the expected grand mean temperature of the earth? Also of the planets Mars and Venus whose orbital diameters are 283 million and 134 million miles, respectively? Assume the bodies to be spheres with uniform surface temperatures.

4. Measurements of temperatures in the large mass of sea water distributed over the surface of the earth indicate a grand mean temperature of 15° C. Assuming that the earth emits and absorbs as a black body, what must be the effective temperature of free space? What is the interpretation of this?

5. What range of temperature would probably be experienced at a position on the moon's equator for a lunar day?

6. The emissivity of the surface of a spherical gondola on a daylight stratospheric flight is 0.6 for all wavelengths. What temperature would exist within the room? Discuss the result for a different emissivity.

7. The temperature of the water in a thermos bottle (full) changes from 91° C. to 90° C. in 20 minutes when the outer shell is at a temperature of 20° C. Find the approximate time required for the change in temperature from 0° C. to 1° C., neglecting any effects due to conduction. Solve first using Newton's law and then again using the Stefan-Boltzmann law.

8. A blackened ball of iron having a diameter of 10 cm. is cooling in an evacuated space whose walls are maintained at 0° C. How long will be required for its temperature to change from 200° C. to 199° C.?

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[45] D. H. Menzel, W. W. Coblenz, and C. O. Lampland, *Astrophys. Jour.*, **63**, 177 (1926).

9. What stellar temperature would result in the emission of radiation such that the wavelength of maximum energy would lie in the x-ray region at, say, 1 Å.? What minimum voltage applied to an x-ray tube would produce this same wavelength?

10. From the above value of the solar constant, calculate the total repulsive force exerted by the sun on the earth, due to radiation pressure? How does this compare in order of magnitude with the gravitational force?

CHAPTER VI

FIRST LAW OF THERMODYNAMICS ENERGY EQUIVALENCE

The fundamental idea of an identity underlying apparently different quantities in the various branches of science was undoubtedly suspected in very early times. The idea of conservation of momentum was firmly established by Newton (1642–1727). It was considerably later that the equivalence of thermal energy and mechanical energy was credited, to the extent that anyone should experiment regarding it. The suspicions of Bacon as well as the pioneer experiments of Benjamin, Count of Rumford,[1] (1798), have already been mentioned on page 42. Rumford, in drilling a cannon, showed a quantitative proportionality between the mechanical work done and the resulting heat communicated to water in thermal contact with the gun cylinder. In concluding his report to the Royal Society of London, Rumford stated, " I am very far from pretending to know how or by what means, that particular kind of motion in bodies which has been supposed to constitute heat is excited, continued and propagated. Even though the mechanism of heat should, in fact, be one of the mysteries of nature which are beyond the reach of human intelligence, this ought by no means to lessen our ardor to investigate the laws of its operation."

The notion of the equivalence of heat and the mechanical energy producing it, as suggested by Rumford and elaborated further by Davy was not generally accepted, however, until after the very precise experiments of Joule, begun about 1840. This principle, that any quantity of mechanical energy is equal to the thermal energy into which it may be transformed, is called the " first law of thermodynamics." The universal acceptance of this principle might be said to date from 1846 when Joule[2] delivered a lecture before the Manchester Philosophical Society entitled " On a New Theory of Heat." Although the ideas presented here had really been stated many times before, this paper and another presentation by Joule before the British Association in the following year were given general recognition.

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[1] Benjamin, Count of Rumford, *Phil. Trans.* **88,** 80 (1798).

[2] J. P. Joule, *Manch. Phil. Soc. Mem.*, **7,** 111 (1846).

The first law of thermodynamics might be expressed very simply as

$$W = JH \tag{1}$$

where W represents the mechanical energy, H the equivalent energy in heat units, and J is termed the "mechanical equivalent." Many experiments have been performed to evaluate this quantity J.

Experiments of Joule on the Mechanical Equivalent of Heat. Beginning in 1840 and reporting finally in 1878, Joule carried out many experiments to obtain the mechanical equivalent of heat, J, with greater and greater certainty. His first result,[3] reported in 1843 at a meeting of the British Association, was a value for J of 883 ft-lb. per British thermal unit (Btu.) (heat to raise the temperature of 1 lb. of water 1° F.). This first apparatus consisted of an electric dynamo rotated by a measured amount of mechanical energy. The output of the machine was dissipated in a resistance immersed in a definite amount of water, elevating the temperature a measured amount.

In 1845 he first described an experiment[4] in which falling weights were made to agitate water in a calorimeter. The potential energy lost by the descending weights, in uniform motion, was set equal to the heat developed in the water. That is,

$$\Delta(mgh) = JM_W(\Delta T) \tag{2}$$

where m is the mass of the falling weight, g is the acceleration of a freely falling body, h is the vertical distance through which the center of gravity of the weight is lowered, M_W is the mass of water whose temperature is elevated by the amount ΔT, and J is the mechanical equivalent of heat. The result reported in this case was that 890 ft-lb. were equivalent to 1 Btu.

This apparatus was improved in form to reduce external friction, and in 1850 the value of 772 ft-lb. was reported as equivalent to 1 Btu. at 60° F. Several other determinations using different methods were made, but they were considered by Joule to be less accurate than the method of the water calorimeter.

The British Association, in setting up practical electrical units, assumed the equivalence of mechanical and electrical energies. Hence if the power to operate an electric generator be known and any losses accounted for, then when it is made to furnish a current I through an electrical conductor of resistance R,

$$P = RI^2 \tag{3}$$

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[3] J. P. Joule, *Phil. Mag.*, **23**, 263 (1843).

[4] J. P. Joule, *Brit. Assoc. Report*, Part 2, p. 31, 1845; *Roy. Soc. Proc.*, **27**, 38 (1878).

The net power P was measured in mechanical units, in ergs per second, and I was measurable in the electromagnetic system in terms of the magnetic field surrounding the conductor. Thus the unit of R could be evaluated. As soon as the new electrical units were established, Joule attempted to check his final value of J by a purely electrical method. Using the British Association unit of resistance and carefully measuring the electric current I and the time t that the current flowed, as well as the temperature change ΔT produced in a known mass of water M_w so that:

$$RI^2t = JM_w\Delta T \tag{4}$$

he obtained the value of 782 ft-lb. per Btu. This was so different from his previously reported value of the mechanical equivalent that he was led to repeat more carefully than ever his previous experiment. He again obtained the value 772.5 ft-lb. per Btu. or 4.155×10^7 ergs per 15° C. calorie. Thus this first British Association unit of resistance was shown unquestionably to be in error. If there were no alternative, then the electrical unit might better have been established on the basis of Joule's result. Fortunately, however, there are other possibilities of establishing the unit of resistance.

An independent absolute method of determining electrical resistance was proposed by Lorenz[5] in 1873. In this method it was shown that resistance could be expressed by measuring a mutual inductance and a time. Many experiments were carried out to establish definitely the value of the absolute unit of resistance in terms of the then generally accepted British Association unit. As a result of several investigations, Rayleigh[6] concluded that the British Association unit was equivalent to 0.98677×10^9 cgs. units, thus indicating an error of more than 1.3 per cent. This value was of considerable weight in establishing the international ohm. Many similar investigations have been carried out by other experimenters.[7]

An apparatus for determining the absolute value of a resistance R is shown in Fig. 75. The solid disk of radius r is made to spin uniformly about an axis at the center of the solenoidal coil. By passing a current I through the resistance R in series with the solenoid and a variable resistance R', the magnetic field may be adjusted to any desired value. Thus the field H is

$$H = 0.4\pi n\, I$$

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[5] L. Lorenz, *Ann. Phys. Chem.*, **149**, 251 (1873).

[6] Lord Rayleigh, *Roy. Soc. Trans.*, **174**, 295 (1883).

[7] W. E. Ayrton and J. V. Jones, *Brit. Assoc. Reports*, 1897; F. E. Smith, *Roy. Soc. Trans.*, **89**, 525 (1913).

where n is the number of turns of wire per centimeter and I is the current in amperes. Between the axis and the periphery of the spinning disk is a constant electromotive force that is applied to the terminals of R through the galvanometer as shown. The disk is run at such a speed and in such a direction that the induced electromotive force e is exactly equal to the potential drop in R. For this the galvanometer reads zero, and the value of e is determined by the time rate of cutting flux $\Delta\phi/\Delta t$, so that

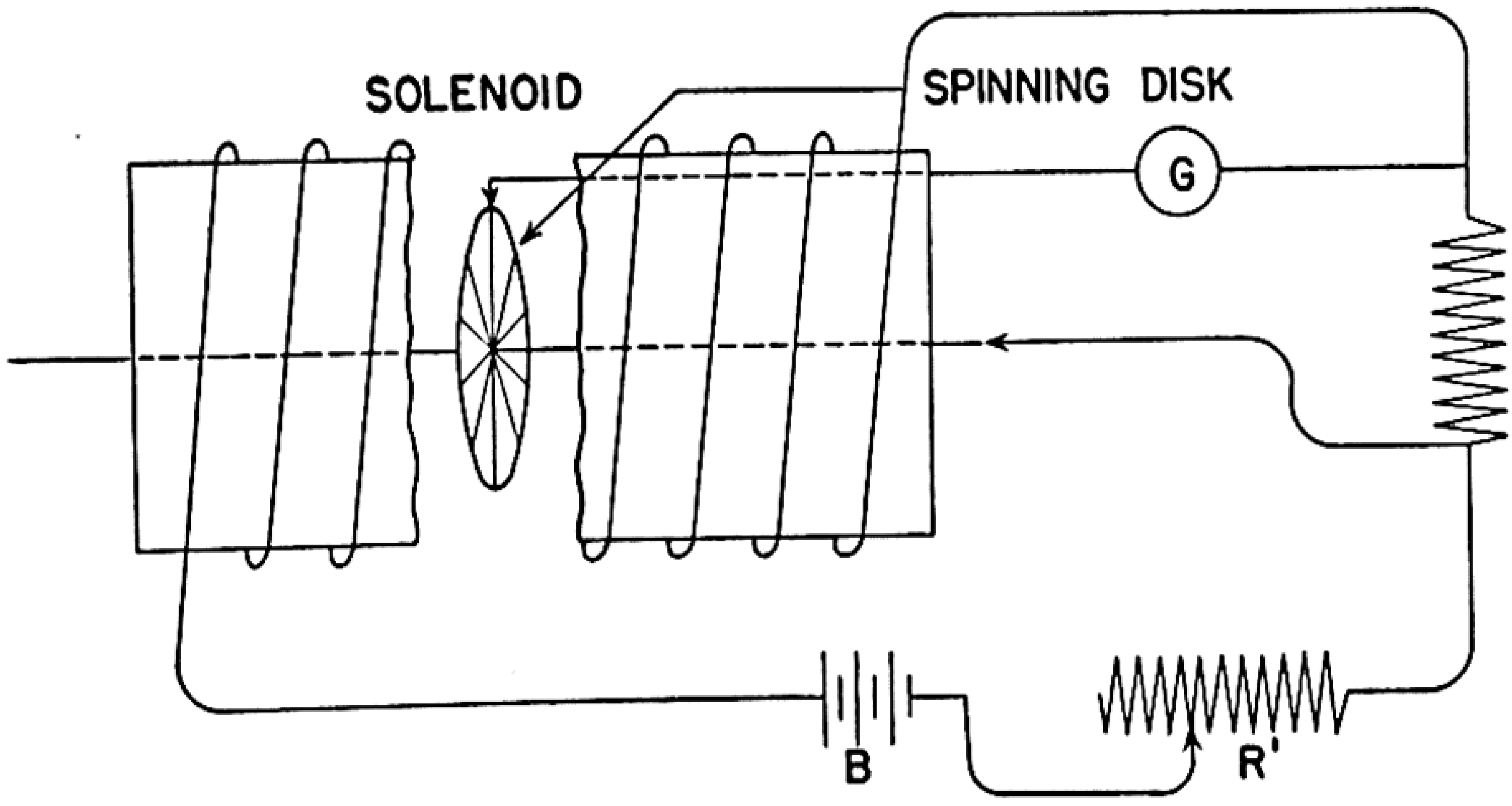

FIG. 75. Apparatus for the absolute measurement of electrical resistance.

$$RI = e = \frac{\Delta\phi}{\Delta t} = B\frac{\Delta A}{\Delta t} = \pi B r^2 f = \pi\mu H r^2 f = 0.4\pi^2 \mu r n f I \qquad (5)$$

where f is the number of revolutions of the disk per second and μ is the permeability of the medium, unity in this case. It then follows explicitly that

$$R = 0.4\pi^2 r^2 n f \qquad (6)$$

in which all quantities on the right side are susceptible of precise measurement.

The more recent experiments of Grüneisen and Giebe[8] indicate that the adopted international ohm is slightly in error. They give as their final result — 1 int. ohm = 1.00051 ohm (10^9 emu.). Birge[9] concludes that the international ohm is equivalent to 1.00048 absolute ohm.

Rowland's Experiment. Joule's work has been followed by many other investigations to determine the mechanical equivalent of heat. Perhaps the most accurate of all these was that of Rowland[10] carried out at the Johns Hopkins University, Baltimore. In this experiment a calorimeter of very large thermal capacity (9 kg. of water) was suspended on a wire. A system of paddles within the calorimeter was rotated by a steam engine. This apparatus is shown in Fig. 76. A counter torque was applied to the outer calorimeter by the weights P and O, keeping its angular displacement always at zero. The elevation in temperature of the calorimeter was measured by mercury thermometers calibrated in terms of the air thermometer.

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[8] E. Grüneisen and E. Giebe, *Ann. Phys.*, **63**, 179 (1920).

[9] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[10] H. A. Rowland, *Proc. Am. Acad. Sci.*, **15**, 75 (1879).

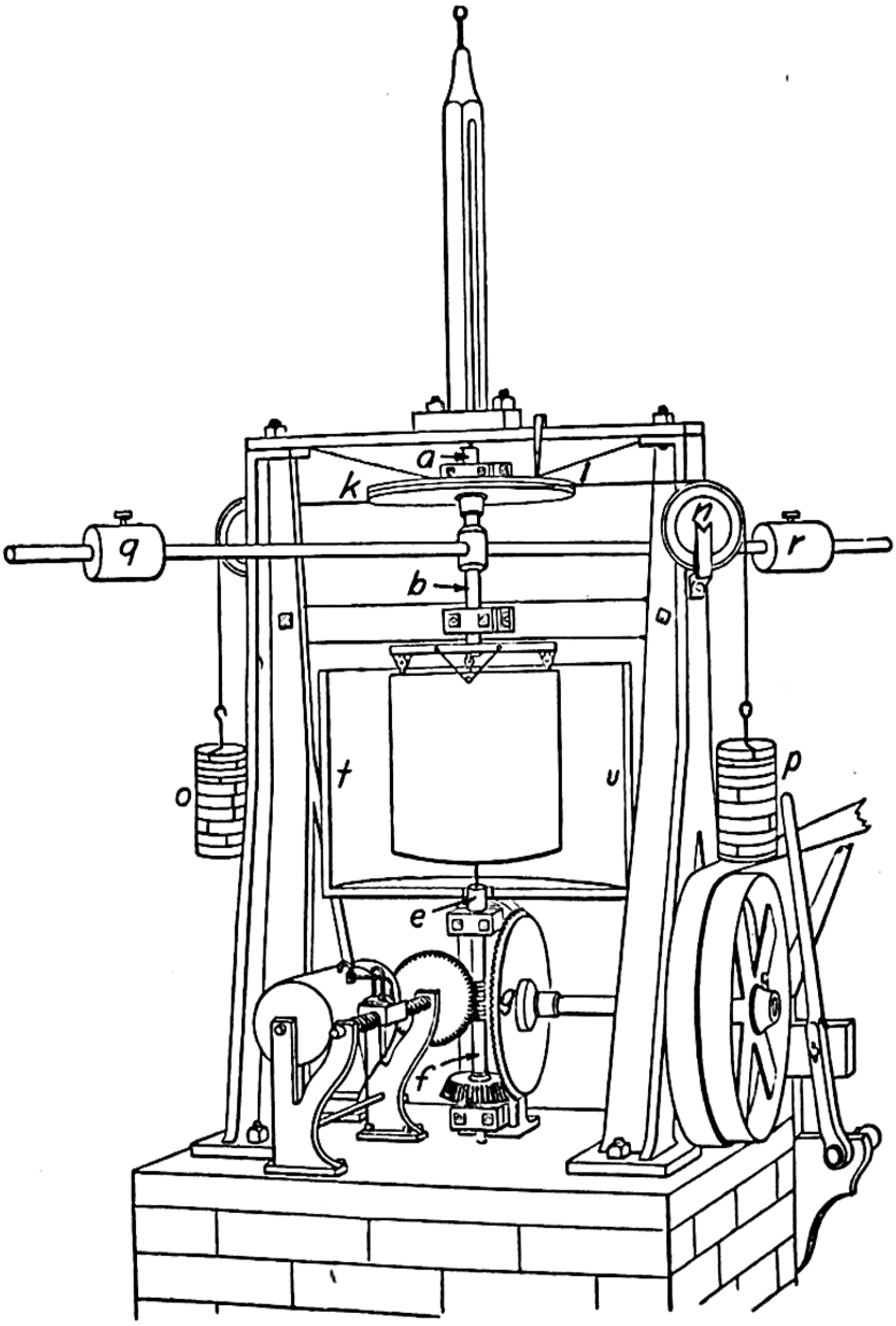

FIG. 76. Apparatus of Rowland for determining the mechanical equivalent of heat.

A comparison of the thermometers used by Rowland and other thermometers calibrated in terms of the normal gas thermometer was carried out by Day[11] at Baltimore. Similar corrections were applied to the observations of Joule. These corrections brought the result of Rowland and that of Joule to an agreement better than ⅕ of 1 per cent. The values of Rowland showed in a striking way the variation in the thermal capacity of water with temperature. In Fig. 77 are pictured the values of the mechanical equivalent obtained by Rowland as corrected by Day, for temperatures from 5° C. to 36° C.

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[11] W. S. Day, *Phys. Rev.*, **6**, 193 (1898).

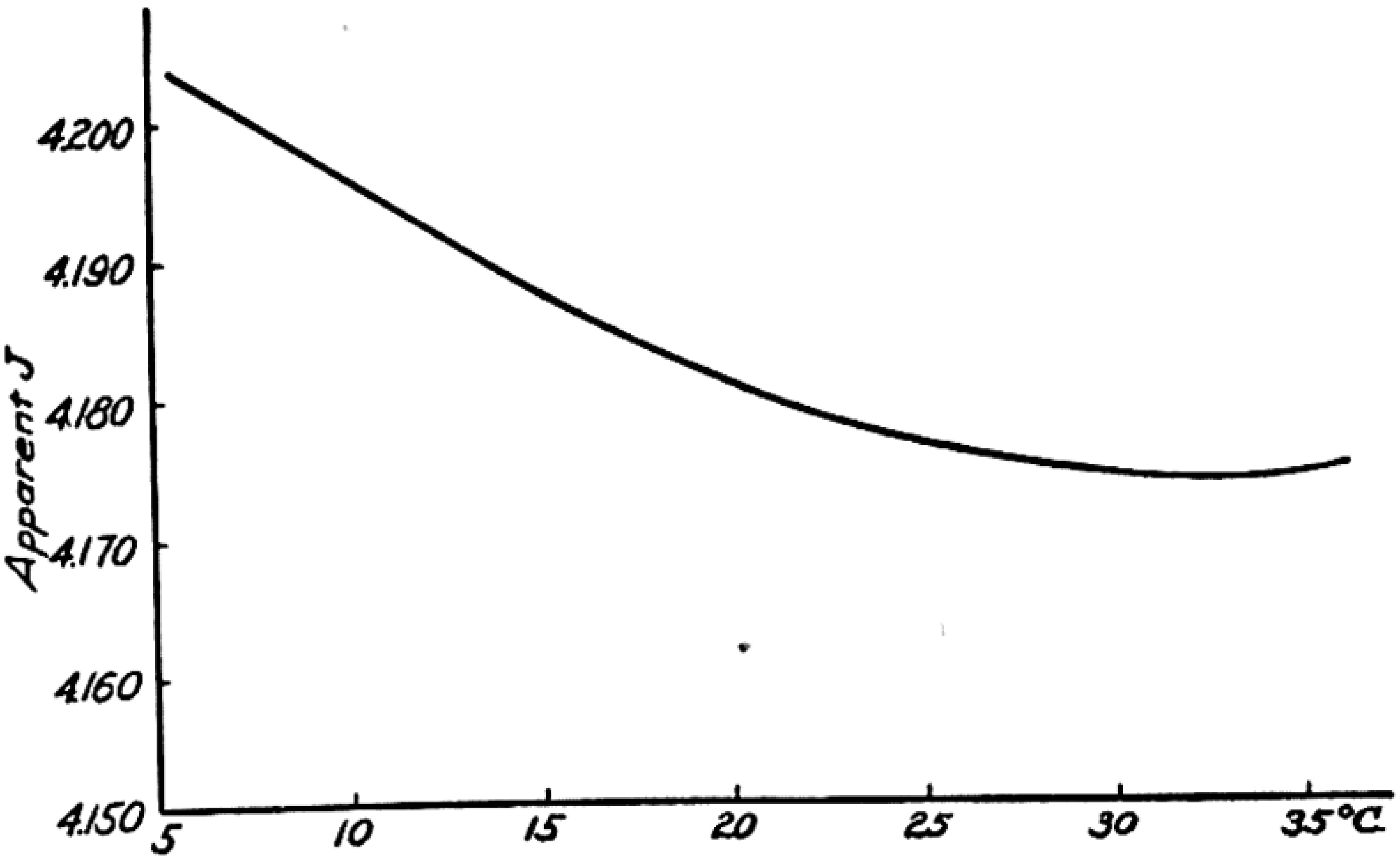

FIG. 77. Variation of J with temperature (Rowland).

Electrical Method. On page 174 is discussed the establishment of the fundamental electrical units. These units having been established independently of any thermal experiment, it becomes permissible to obtain from them the value of the mechanical equivalent of heat. This has been carried out by many experimenters, one of the first being Griffiths,[12] after the establishment of the international ohm. With the excellent thermos flasks now available to reduce heat losses by radiation and with electrical instruments calibrated in terms of the international units, which in turn are related to the absolute units, it is readily possible to express J with considerable definiteness. If E denotes the voltage, I the steady current flowing for the time t, M_w the water equivalent of the calorimeter and its contents whose temperature is changed by the amount ΔT, then

$$EIt = JM_w\Delta T$$

The exactness of the value of J depends upon the following uncertainties in the electrical units, which as determined by H. L. Curtis[13] and R. W. Curtis and edited by Birge[14] are

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[12] E. H. Griffiths, *Phil. Trans.*, **184A**, 361 (1893).

[13] H. L. Curtis and R. W. Curtis, *U. S. Bur. of Standards, Jour. of Res.*, **12**, 685 (1934).

$$1.00034 \pm 0.00003 \times 10^8 \text{ emu. potential} = 1 \text{ international volt} \tag{7}$$

$$0.99986 \pm 0.00002 \times 10^{-1} \text{ emu. current} = 1 \text{ international ampere} \tag{8}$$

$$1.000481 \pm 0.00002 \times 10^9 \text{ emu. resistance} = 1 \text{ international ohm} \tag{9}$$

Thus 1 international joule is equivalent to 1.00020 ± 0.00004 absolute joules.

Method of the Rotating Magnetic Field. If a mass of metal is made to move with respect to a magnetic field, then " eddy " currents will be set up in the metal. The metal will experience a force tending to make it move along with the field. This principle has been used in an apparatus[15] to determine the mechanical equivalent of heat. As originally used, a large electromagnet in the form of a hollow shell was constantly excited through slip rings and rotated at a high speed by an electric motor. Inside the hollow magnet was a Dewar flask in which was supported a mass of metal on a torque arm. In the apparatus shown in Fig. 78, the advantage of the thermos flask is exchanged for the larger torque to be obtained by reducing the reluctance of the magnetic circuit. The rotating magnetic field is accomplished by using the stator of a three-phase induction motor. The rotor, in addition to the metal, contains a large volume of water, so that large amounts of energy can be transformed with the radiation loss kept at a small value. The rotor is held from moving by the counter torque τ. The angle θ may be computed from the time of excitation of the field

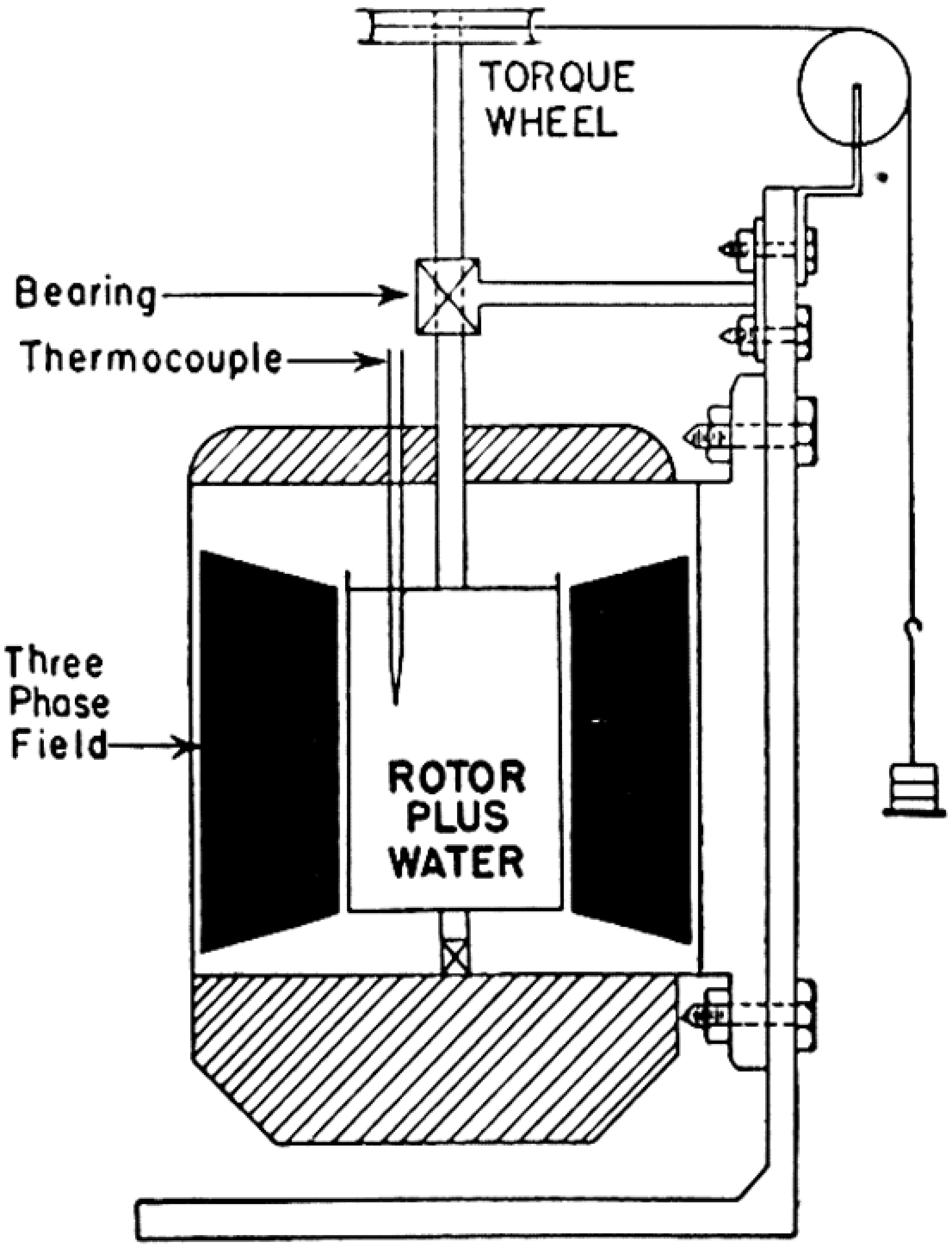

FIG. 78. Mechanical equivalent by rotating magnetic field.

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[14] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[15] J. M. Cork, *Jour. Opt. Soc. Amer.*, **14**, 99 (1927).

and the frequency of the current. The mechanical energy W, which is the product of the torque τ and the angular displacement θ, may be expressed in terms of the equivalent heat units H as

$$W = \tau\theta = JH = J\,M_w\Delta T \tag{10}$$

where M_w is the water equivalent of the rotor and ΔT its change in temperature. Hence

$$J = \frac{\tau\theta}{M_w \ \Delta T} \tag{11}$$

A method similar in principle was reported almost at the same time by Laby and Hercus.[16] Many other experiments to determine J, too numerous to be described, have been carried out. References to a few[17] of the original papers are given. The electrical method has been employed with perhaps the greatest accuracy by Jaeger and von Steinwehr.[18] In reviewing the present available data, Birge[19] concludes for the most probable value:

A 15° calorie = 4.1847 international joules = 4.1855 absolute joules.

Energy and Mass. From the relativistic considerations of Einstein,[20] the following result of the greatest importance was formulated:

" Every quantity of energy of any form whatever represents a mass which is equal to this same energy divided by C^2, where C is the velocity of light; and every quantity of energy in motion represents momentum."

Thus if energy is radiated from a body, the mass of that body must be decreasing, or conversely, if in any phenomenon a decrease in mass is observed, then a definite amount of radiation must have escaped from the body. This change in energy ΔE in ergs is related to the accompanying change in mass ΔM in grams, as follows:

$$\Delta E = \Delta M \cdot C^2 \tag{12}$$

The atomic weight of the neutral hydrogen atom as reported[21] from observations made by the mass spectograph is 1.00813. On the same scale the atomic weight of the electron is 0.000548, and the weight of the neutron is 1.00897. Accordingly, if we regard the heavier elements as built from these fundamental particles, then an element such as oxygen of mass 16 would consist of 8 neutral hydrogen atoms and 8 neutrons. The expected atomic weight would therefore be

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[16] T. H. Laby and E. O. Hercus, *Phil. Trans.*, **227A**, 63 (1927).

[17] A. Schuster and W. Gannon, *Phil. Trans.*, **186A** (1895); H. L. Callendar and H. T. Barnes, *Phil. Trans.*, **199A**, 1902. W. E. Bousfield and W. R. Bousfield *Phil. Trans.*, **211A**, 236 (1911).

[18] W. Jaeger and H. von Steinwehr, *Ann. Physik*, **64**, 305 (1921).

[19] R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[20] A. Einstein, *Ann. Physik.*, **20**, 627 (1906).

[21] K. T. Bainbridge, and E. B. Jordan, *Phys. Rev.*, **50**, 282 (1936).

$$8(1.00813) + 8(1.00897) = 16.1341 \tag{13}$$

Comparing this with the true value 16.0000 assumed for the neutral oxygen atom one observes a loss in mass each time an oxygen atom is formed of 0.1341 times the weight in grams of the hydrogen atom $(1.6734 \times 10^{-24}$ gm.).

If this atomic building takes place in one process, then the energy of the complete system will be decreased by a definite amount ΔE which may be calculated from equation 12. This loss in energy will be radiated as an electromagnetic wave of a single definite frequency ν. The frequency ν, according to a postulate of Bohr,[22] is related to the energy change ΔE as follows, where h is the Planck constant of action, C is the velocity of light, λ is the wavelength of the radiation, and Δm the change in mass.

$$\Delta E = h\nu = h\frac{C}{\lambda} = \Delta m \cdot C^2 \tag{14}$$

Hence for the particular problem of the oxygen atom

$$\Delta E = 2.018 \times 10^{-4} \text{ erg} \tag{15}$$

and

$$\lambda = \frac{(6.624)10^{-27} \cdot 3 \cdot 10^{10}}{2.018 \cdot 10^{-4}} = 0.0000984 \times 10^{-8} \text{ cm.}$$

$$= 0.0000984 \text{ Å} = 0.0984 \text{ X units} \tag{16}$$

Wavelengths of this order were reported by Millikan[23] to be present in cosmic radiation, corresponding to the building of four of the most common elements in the universe — helium, oxygen, silicon, and iron. Primary cosmic radiation is, however, now believed to consist mainly if not entirely of particles.

The energy associated with the process of building heavier atoms from protons and neutrons, if not allowed to escape (i.e., if completely absorbed by similar neighboring atoms formed in the same way), would be sufficient to produce an extremely high elevation of temperature. Such processes may be occurring in stellar bodies under high pressure. If C_v is the specific heat of a substance, then the thermal capacity per atom of that substance is $A \times C_v \times 1.6734 \times 10^{-24}$ cal. per deg. C., where A is the atomic weight. The released energy per atom ΔE would thus result in a rise in temperature ΔT equal to:

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[22] N. Bohr, *Phil. Mag.*, **26**, 1 (1913).

[23] R. A. Millikan, *Phys. Rev.*, **32**, 533 (1928).

$$\Delta T = \frac{\Delta E \text{ per atom}}{\text{Thermal capacity per atom}} = \frac{\Delta m \cdot C^2}{J \times A \times C_v \times M_H} \tag{17}$$

M_H is the mass of the hydrogen atom in grams and J is the mechanical equivalent of heat. For monatomic oxygen

$$\begin{aligned} \Delta T &= \frac{2.018 \times 10^{-4}}{4.185 \times 10^7 \times 16 \times 0.186 \times 1.6734 \times 10^{-24}} \\ &= 96.8 \times 10^{10} \text{ deg. C.} \end{aligned} \tag{18}$$

In forming the oxygen molecule from these oxygen atoms, still more energy is released.

It is thus apparent that the very highest temperatures that are known to exist in stellar bodies might be a natural consequence in a universe having in the beginning only cold hydrogen nuclei endowed with a willingness to combine.

Thus Bethe[24] concludes that, at a sufficient depth below the surface in our sun where the density is 80 gm. per cm.^{3} and the hydrogen content is 35 per cent by weight, there exists a temperature of 2×10^7 °K. Under these conditions the production of heavy hydrogen from protons with the emission of a positron is sufficient alone to yield continuously 2 ergs per gram per second. In addition to this reaction, other cyclic nuclear interactions are proposed in which the elements carbon, nitrogen, and oxygen serve as catalysts in forming helium from hydrogen. In this cycle beginning with a carbon isotope of mass 12, one proton at a time is added. This process is sometimes accompanied by the emission of positrons so that ultimately the product nucleus oxygen of mass 16 is attained. This, in its excited state emits an alpha particle (helium nucleus), together with a carbon atom as existed in the beginning. An estimate is made that this process yields continuously about 100 ergs per gram per second under the above conditions. This is sufficient to account for the present total radiation from the sun..

In radioactive processes when heavy elements decompose into those of lesser atomic weight with the emission of α, β, and γ rays, heat is again liberated. For 1 gm. of radium in equilibrium with its products of disintegration, a quantity of heat equivalent to 139.6 cal. per hour is released.[25] If completely absorbed in the gram of substance this is a sufficient amount to elevate its temperature approximately 500° C. Thus to have the liberation of energy at the continuous rate of one kilowatt, a mass of radium of 6,140 gm. would be required.

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[24] H. A. Bethe, *Phys. Rev.*, **54**, 248 (1938); **55**, 434 (1939).

[25] I. Zlotowski, *Jour. Phys. Radium*, **6**, 242 (1935).

An estimate of the age of the earth was made by Lord Kelvin. In his determination he observed the present gradient of temperature at the surface and he postulated the original temperature of the surface to be 3,900° K. Knowing the diffusivity of the earth's crust, he was able to calculate the time that would be required to attain the present condition of temperature and found it to be about forty million years. In the light of the above-mentioned possible internal sources of heat, such estimates are meaningless. An estimate may now be made of the age of the sun by considering the present abundance of helium together with its rate of formation. Such estimates indicate an age of several billion years.

Heats of Combustion — Solids. The formation of a chemical compound from more elementary constituents is in general accompanied by the release of a definite amount of heat per unit mass of substance formed. For fuels, this quantity of heat released when unit mass of the substance unites with the requisite amount of oxygen is called the "heat of combustion." There are in general two types of apparatus by which this quantity may be measured for the solid and liquid forms of fuel. In one form of calorimeter called the bell type, the specimen is contained in a submerged bell and is burned in an oxygen atmosphere at normal pressure. The oxygen gas is made to enter continuously in a manner similar to the principle used in collecting gas over water. The heat evolved raises the temperature of the water surrounding the submerged bell.

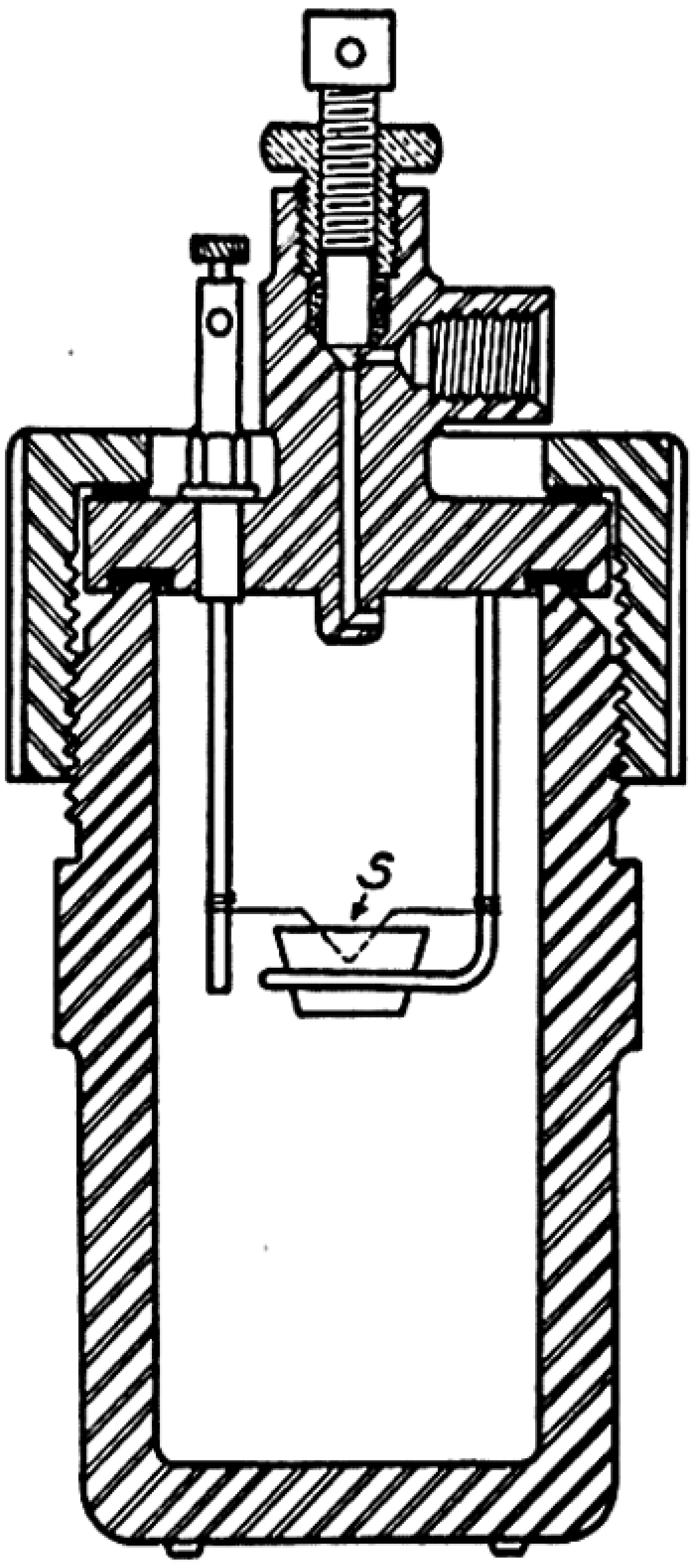

Fig. 79. The bomb calorimeter.

In the other form of calorimeter called the bomb type, the fuel is placed in a strong-walled gas-tight container made of a non-corrosive metal. A small specimen S of the fuel, together with a sufficient amount of oxygen (usually several atmospheres), is sealed in the bomb, as shown in Fig. 79, and the whole immersed in a calorimeter containing water. By heating electrically to red heat a fine wire placed in the bomb, the combustion takes place instantaneously.

A Beckmann thermometer is very well adapted to observe the rise in temperature ΔT in the outer calorimeter, although an electrical resistance thermometer may be preferred. If H.C. denotes the heat of combustion, m the mass of the fuel burned, and M_w the water equivalent of the calorimeter, then:

$$(\text{H.C.})m = M_w \cdot \Delta T + \text{Losses of heat} \tag{19}$$

The bomb calorimeter is often objected to, on the ground that the fuel is here oxidized in a manner unlike that used in actual practice, and hence the results obtained may be quite different. The decomposition products of most coals contain certain active corrosive agents so that the bomb, if made of steel, is often lined with porcelain, platinum, or gold, and should be cleaned after each test.

Gases. The heat of formation of chemical compounds from gaseous constituents is a quantity often desired. This is particularly true for the oxidation of gaseous fuels. Calorimeters of many types have been developed for the measurement of this quantity. These are generally continuous-flow devices, in which a constant gas flame communicates its entire heat to a vessel through which a uniform flow of water is circulating. Figure 80 represents a sectional view of a typical device of this character. In the steady state, the difference in temperature ΔT between the inflowing and the outflowing water is observed. This quantity, together with the rates of flow of gas and of water, suffices to determine the heat evolved per unit mass or per unit volume of gas. In actual practice certain corrections need be applied. One of these corrections is necessary because in the combustion process water vapor is formed. This vapor in passing through the tortuous path taken by

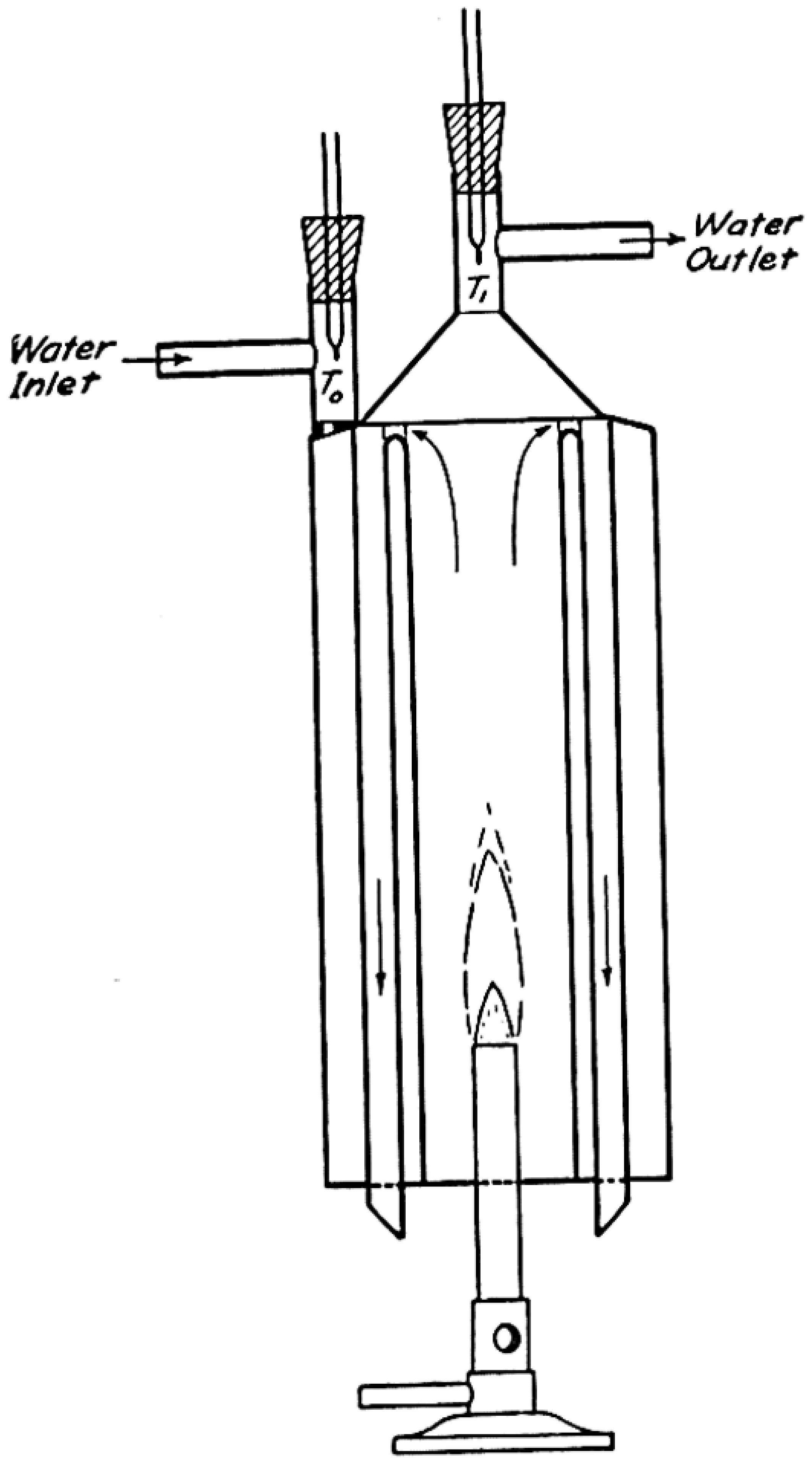

FIG. 80. Calorimeter to determine the heat of combustion of gaseous fuels.

the waste gases gives up its latent heat of condensation to the circulating water and is trapped and measured as liquid water. Since in the actual use of fuel gas this quantity of heat in general would be lost in the flue gases, it is conventional practice in certain groups to subtract its heat content from the apparent gross heat value of the gas, giving the net heating value. If dV/dt represent the volume that flows per second for both the water and the fuel gas, then

$$\text{Heat of combustion in } \frac{\text{calories}}{\text{gram}} = \frac{(dV/dt)_w(\text{Density})_w \times (\Delta T)_w}{(dV/dt)_g\ (\text{Density})_g} \tag{20}$$

These overall measurements are, of course, the summation of the energies of reaction associated with the formation of the very great number of individual molecules.

Thus if it is observed that A calories of heat are released when 1 gm. of a substance is burned in an excess of another substance, then the energy per molecule formed is equal to qA/N, where N represents the number of atoms of the first substance in 1 gm. and q is the number of atoms of the first substance in the molecule that is formed.

This energy would be radiated as an electromagnetic wave and may be expressed in several ways by employing the Bohr frequency postulate for the radiation. That is, the radiation should be expected to have a characteristic frequency ν or wavelength λ as given in equation 15. Thus the energy of formation per molecule is

$$\frac{qA}{N}\text{ calories} = \frac{JAq}{N}\text{ ergs} = h\nu = h\frac{c}{\lambda} = 1\frac{Ee}{300} \tag{21}$$

where ν is the frequency of the radiation and λ is the wavelength. The factor 1/300 is introduced to convert volts to electrostatic units so that the result is in ergs. If e is the charge of the electron in electrostatic units then the energy sent out might be referred to as radiation of E volts. This means that, to impart to an electron of charge e an equivalent amount of energy, it must fall through a difference of potential E. One electron volt is equivalent to 1.602×10^{-12} ergs.

The heats of formation of many compounds as well as the heats of association or dissociation of molecules into atoms have now been measured. This information is of importance in modern theories of the structure of matter.

Heat from the Fission of Uranium. Less ardent than the alchemists and the inventors of " perpetual motion " devices, but more realistic have been the scientists conducting researches leading to the more effective utilization of our stores of energy. With the discovery in

1939 by Hahn[26] and Strassmann that the nucleus of the uranium atom could be made to break into two heavy particles, and the subsequent[27] observations that each such disintegration was accompanied with the release of about 185 million electron volts, a new source of energy was envisioned. The natural isotopes of uranium are 234 (0.006%), 235 (0.710%), and 238 (99.28%). It was soon apparent that the isotope of mass 235, comprising only about 1/140 of the total, would disintegrate by the addition of a single thermal neutron of negligible energy. Moreover, in the fission process more neutrons were liberated, so that such a chain reaction would go on with an accelerated pace if the isotope 235 were isolated. To produce fission in the isotope of mass 238 requires a neutron of about 1.5 million electron volts. This isotope, however, has the ability to absorb effectively the neutrons formed by the fission, leading only to a radioactive isotope of mass 239, of half-life 23 minutes. The problem that must be solved is, then, either to isolate the isotope 235, or to contrive to prevent the absorption by the isotope 238 of the neutrons formed.

If the ultimate solution of this problem allows the complete utilization of the energy of both isotopes, then from 1 gm. of uranium containing 25.3×10^{20} particles an amount of energy approximately equal to 80×10^9 joules (watt-seconds) would be obtained. This would be equivalent to the output of a 1,000-kilowatt machine operating for one day.

The Conservation of Energy and the Neutrino. Although the law of conservation of energy has always been unquestioned in macroscopic processes, there has on occasion[28] arisen doubt regarding its absolute truth when applied to an individual process such as the disintegration of a nucleus. This question is particularly pertinent in considering the beta spectra of radioactive bodies. Any reasonable model of the nucleus would allow only discrete energy levels and absorption or emission should be expected always to involve the gain or loss of a definite amount of energy. Although this is true for α and γ rays, it does not apply to the β spectra. Instead, the electrons are observed to have a continuous distribution in energy, from zero up to a certain definite maximum. One has then the alternative of abandoning the principle of conservation or of postulating the existence of some other type of radiation, emitted with the β particle and sharing in the energy so that the sum of its energy plus that of the electron is a constant.

A crucial calorimetric experiment to measure the average thermal energy of the β particles was carried out by Ellis and Wooster.[29] Radium E emits electrons with a maximum energy of 1,050 kev., and with an average energy of about 390 kev. In the thermal measurement of the energy an average value of 350 ± 40 kev. was observed. It was accordingly concluded that the balance of the energy must be carried off by some undetectible radiation. To satisfy this need a new elementary particle was postulated. It must be of negligible mass and without electric charge and is called a neutrino. In this way any reflection on the validity of the law of conservation of energy can be avoided.

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[26] O. Hahn and F. Strassmann, *Naturwiss*, **27**, 11, 89, 163 (1939).

[27] M. Henderson, *Phys. Rev.*, **58**, 774 (1940).

[28] N. Bohr, H. A. Kramers, and J. C. Slater, *Zeit. Phys.*, **24**, 69 (1924).

QUESTIONS AND PROBLEMS

1. To dissociate H_2 into $H + H$ requires 4.42 volts. What must then be the heat of formation of H_2 in calories per gram? Discuss this in connection with the technique of welding by atomic hydrogen.

2. When 1 gm. of hydrogen is burned in chlorine, 22,030 cal. of heat are liberated. If HCl vapor is broken into normal H_2 and Cl_2 by absorption of radiation in a single step, what critical absorption frequency would be observed? Express also in terms of wavelengths and volts.

3. If an atom of nitrogen is built up of hydrogen atoms and neutrons in one step, what wavelength radiation should accompany the process? Atomic weight of nitrogen is 14.0074 and of hydrogen is 1.00813.

4. Refute the " caloric " theory of heat.

5. What quantity of butter (6,000 cal./gm.) would supply the energy needed for a 200-lb. man to ascend to the summit of a 500-ft. hill?

6. Demonstrate the hypothetical economic advantage in heating by uranium at $2 per lb. compared with coal at $4 per ton, (*a*) using only isotope 235 and (*b*) using both isotopes. Assume an energy of 5 electron volts to be released for each molecule of carbon dioxide formed.

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[29] C. D. Ellis and W. A. Wooster, *Proc. Roy. Soc.*, **117A**, 109 (1927).

CHAPTER VII

THE STATE OF MATTER

Solid, Liquid, and Gas: Definitions. The arrangement of atoms in crystalline solids is now very definitely revealed by x-ray diffraction patterns. This information establishes the fact that in these substances an atom is permanently associated with a definite lattice point about which it may execute vibratory motion. If a large single crystal of a substance be pulverized and then packed in a mold to form a body, the result is a crystalline aggregate which typifies the structure of most ordinary crystalline substances. The finer the pulverization of the crystal before packing, the more amorphous the resulting substance.

Another criterion by which a distinction may be made between crystalline and amorphous substances is the definiteness of the melting point of the substance. Lindemann has postulated that at the melting point the amplitude of the vibratory motion of the lattice particles is of the order of the distance between the particles. Since in a single crystal of appreciable size every particle is under essentially the same conditions, when the orderly arrangement of one particle is disturbed, so also is that of every other. This condition would result in a definite melting point. However, if the process of pulverization is carried far enough, a large percentage of the particles find themselves on the surface of the crystalline grains and these particles are in a different field of force from those particles in the interior of the granules. The variation in the grain size then might be expected to introduce the possibility that the orderly arrangement might break down in one part of the material before it would in another. This would result in a melting point not sharply defined but extending over a range in temperature of a few degrees.

Upon the breakdown of the orderly array of the crystalline lattice, the motion of any individual particle changes from one of vibration to one of translation, traveling with approximately uniform motion between successive elastic impacts with other particles. This type of uniform motion characterizes the particles of both liquids and gases. In the liquid, however, attractions between particles must be such as to result in the formation of a free surface.

Most processes in nature take place in such a direction that the potential energy of the system tends toward a minimum value. A heated liquid in cooling through its freezing point has a readjustment in the arrangement of its particles such that a definite amount of energy is set free. This quantity of energy released per gram, when the state changes, with no change in temperature, is called the heat of fusion of the substance.

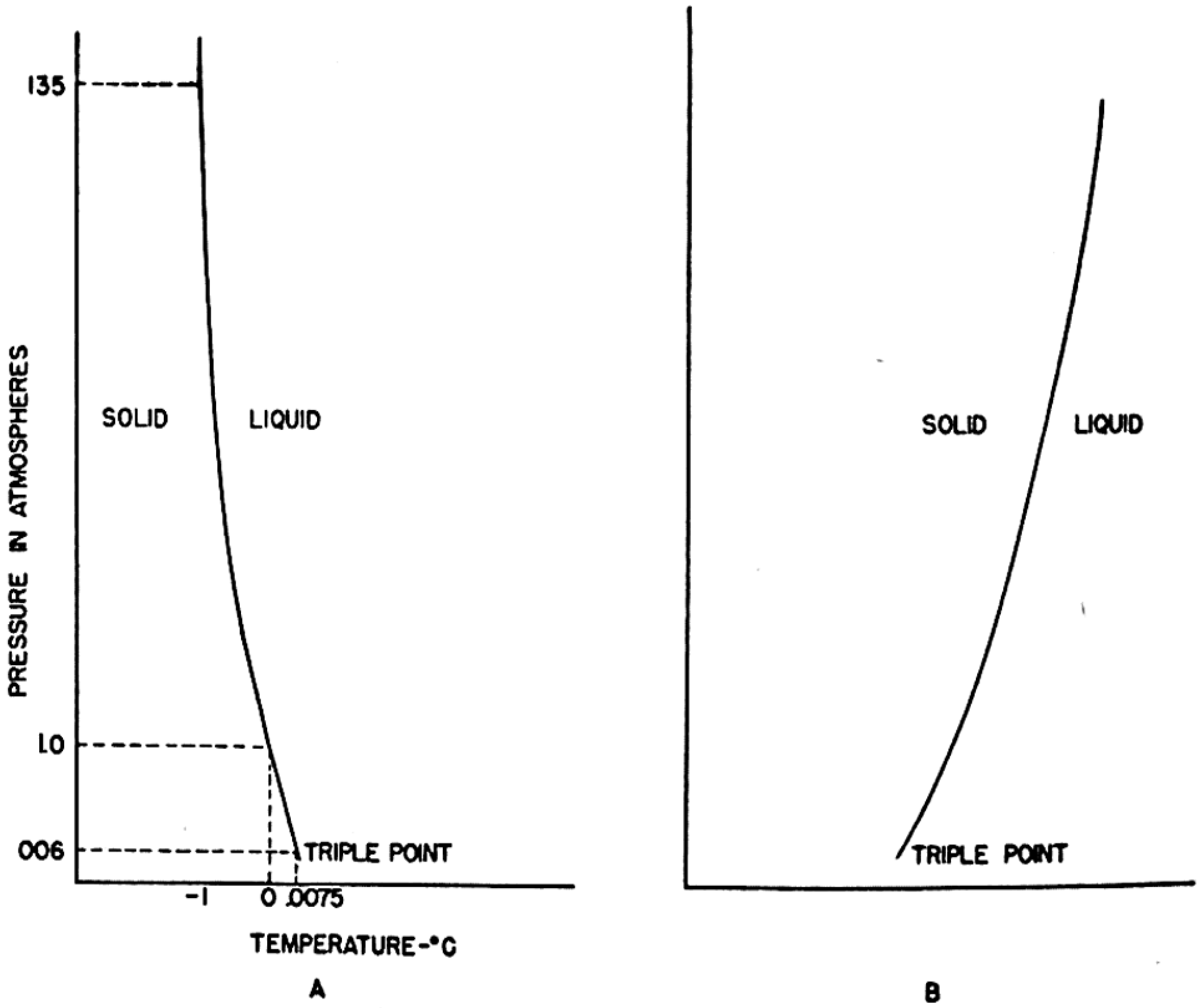
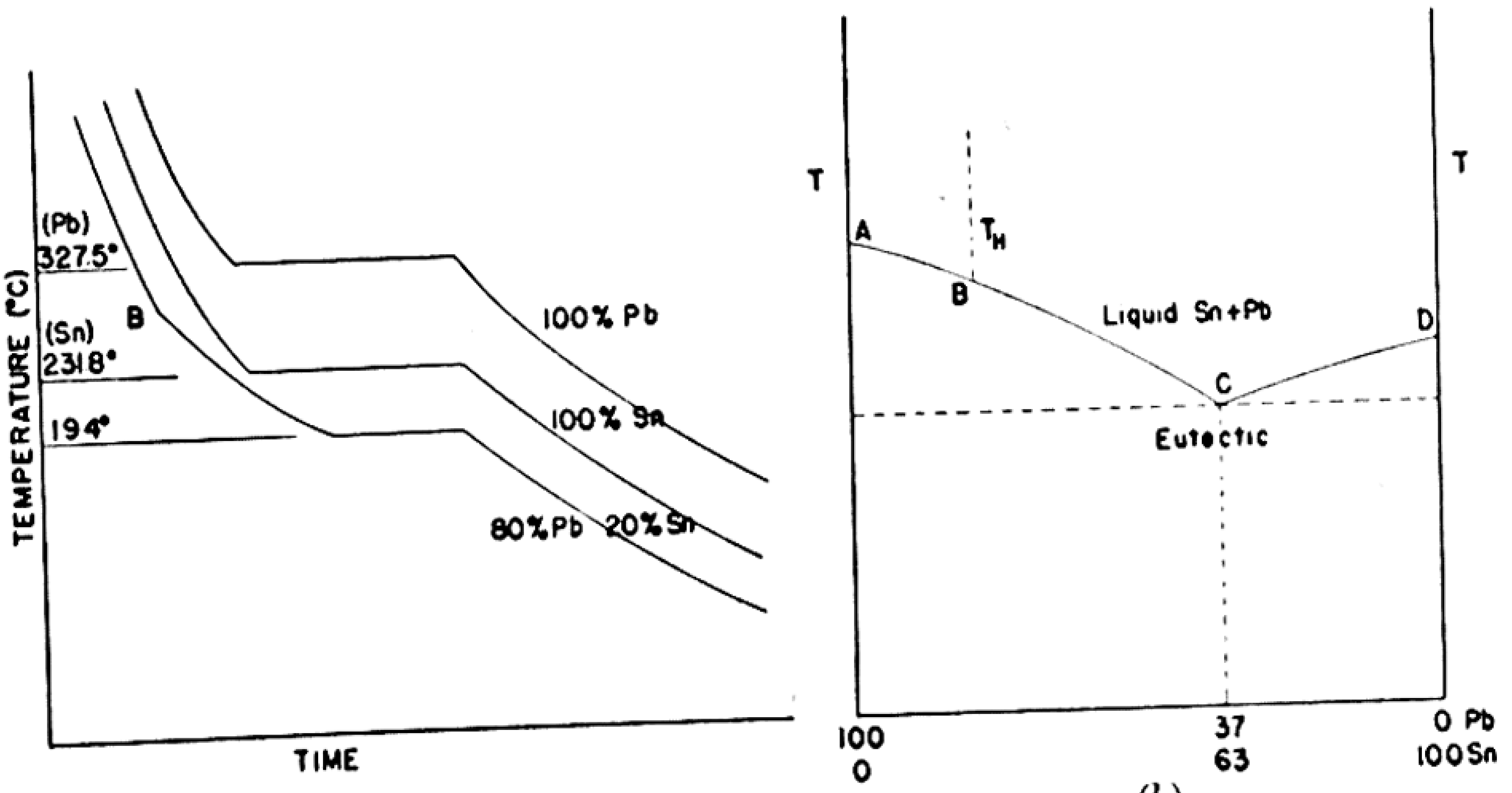


FIG. 81. Change in melting point with pressure: *A*. Water. *B*. Most other solids.

Effect of Pressure upon the Melting Point. When a definite mass of liquid transforms into a solid, a definite change in volume occurs. This may be either an increase or a decrease depending upon the substance. For most materials the change into the solid phase is accompanied by a decrease in volume. Notable exceptions are water, bismuth, and perhaps iron. If the volume of the solid is greater than that of the liquid at the same temperature, then an increased pressure would favor the liquid phase or lower the freezing point. The effect of an increase in pressure upon the melting point for the two types of substances is shown in Fig. 81. Curve *A* represents the performance of water. The curve is drawn somewhat distorted so as to show the lower end more clearly. A pressure change of about 135 atmospheres will lower the freezing point 1 deg. C. The behavior of most common substances is shown in curve *B*. For solids obeying the *A* relationship a sufficient increase in pressure will result in a transformation into the liquid phase. Additional pressure may, however, finally transform the liquid into the solid phase again. Curves by Bridgman showing this transformation for water are reproduced in Fig. 103.

Impurities and the Melting Point. The addition of a slight amount of impurity, regardless of its nature, acts to lower the melting temperature of a substance. This result is in accord with expectations from the kinetic model. The interpenetration of foreign particles in the solid lattice would, upon heating, result in the disruption of the orderly atomic arrangement at a lower temperature.



(*a*) (*b*)

FIG. 82. Cooling curves and equilibrium diagram for a two-component system.

For many substances the alteration of the melting point is proportional to the amount of the impurity present, up to a certain limit. For two constituents the particular percentage combination having a minimum melting point is called a eutectic mixture. If one of the components is water, then the mixture at the minimum temperature is termed a cryohydrate. The variation in the melting point of a mixture of lead and tin with changes in the percentage of the components is illustrated in Fig. 82*b*. Starting with constituents whose melting points are 231.8° C. and 327.5° C. respectively, a eutectic of melting point 194° C. is possible. By combining this eutectic with a third metal bismuth (M.P. 271.3° C.), an alloy may be obtained with a melting point as low as 94° C. This process may be extended farther by introducing additional constituents to produce alloys with extremely low melting points. Thus Wood's metal which consists of 50 per cent bismuth, 25 per cent lead, 12.5 per cent antimony, and 12.5 per cent cadmium melts at 65.5° C.

Experimental. The complete equilibrium diagram shown in Fig.

82*b* can be approximately drawn, simply by noting the cooling curves for two different mixtures of the two components. Thus in Fig. 82*a* are shown cooling curves for the two pure substances and for a mixture of 80 per cent lead and 20 per cent tin. As this hot mixture at an original temperature T_H cools to the point shown as B, the component lead begins to freeze out. The latent heat released in this process causes the mixture to cool less rapidly. Finally when the composition of the eutectic is attained the residue freezes, keeping the temperature constant until solidification is complete. By repeating this process, starting with a mixture of 20 per cent lead and 80 per cent tin, the tin will freeze out first. The continued freezing leads again to the same eutectic mixture. Smooth curves drawn through these observed temperatures allow the completion of the figure as shown.

Transition Temperatures in Solids. In attaining the state of minimum potential energy, many heated solids will upon cooling exhibit a sudden change in their crystalline structure at certain definite temperatures. This change in atomic arrangement is generally accompanied by the release of a definite amount of heat per gram of the substance, similar to the heat of fusion. This allows the detection of the transition temperature by observing the rate of cooling. The body will cool less rapidly in passing through the transition point because of the latent heat set free. It often happens that on either side of this transition temperature the physical properties of the substance are very different. A cooling curve as obtained for pure iron, demonstrating the presence of these transition points, is shown in Fig. 83. At 1,539° C. the liquid freezes into a solid termed the δ phase. This form of iron has been found to possess a body-centered cubic structure. Upon cooling through a temperature about 1,405° C. this form changes over into the γ form, which possesses a face-centered cubic structure. X-ray investigations[1] show that upon further cooling the γ face-centered structure changes over at about 900° C. into a β form having a body-centered cubic structure. This in turn changes to the α form at about 770° C. with no change in crystalline type. As a liquid may often be supercooled below its normal freezing temperature without solidifying, so also may the solid in one phase be cooled below the normal transition temperature without the transformation occurring. Thus, by quenching from temperatures above 900° C. γ iron with the desirable properties associated with the face-centered structure, may be made to exist at normal room temperature. By proper alloying, it may be made to retain the characteristics of the higher-temperature phase indefinitely. The crystallization of glass or molasses candy with age are striking examples of retarded transformation. These transition temperatures are affected by changes in pressure and by impurities in the same way as are normal freezing points.

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[1] A. Westgren, *Jour. Iron Steel Inst.* (*London*), **103**, 303 (1921), *et seq.*

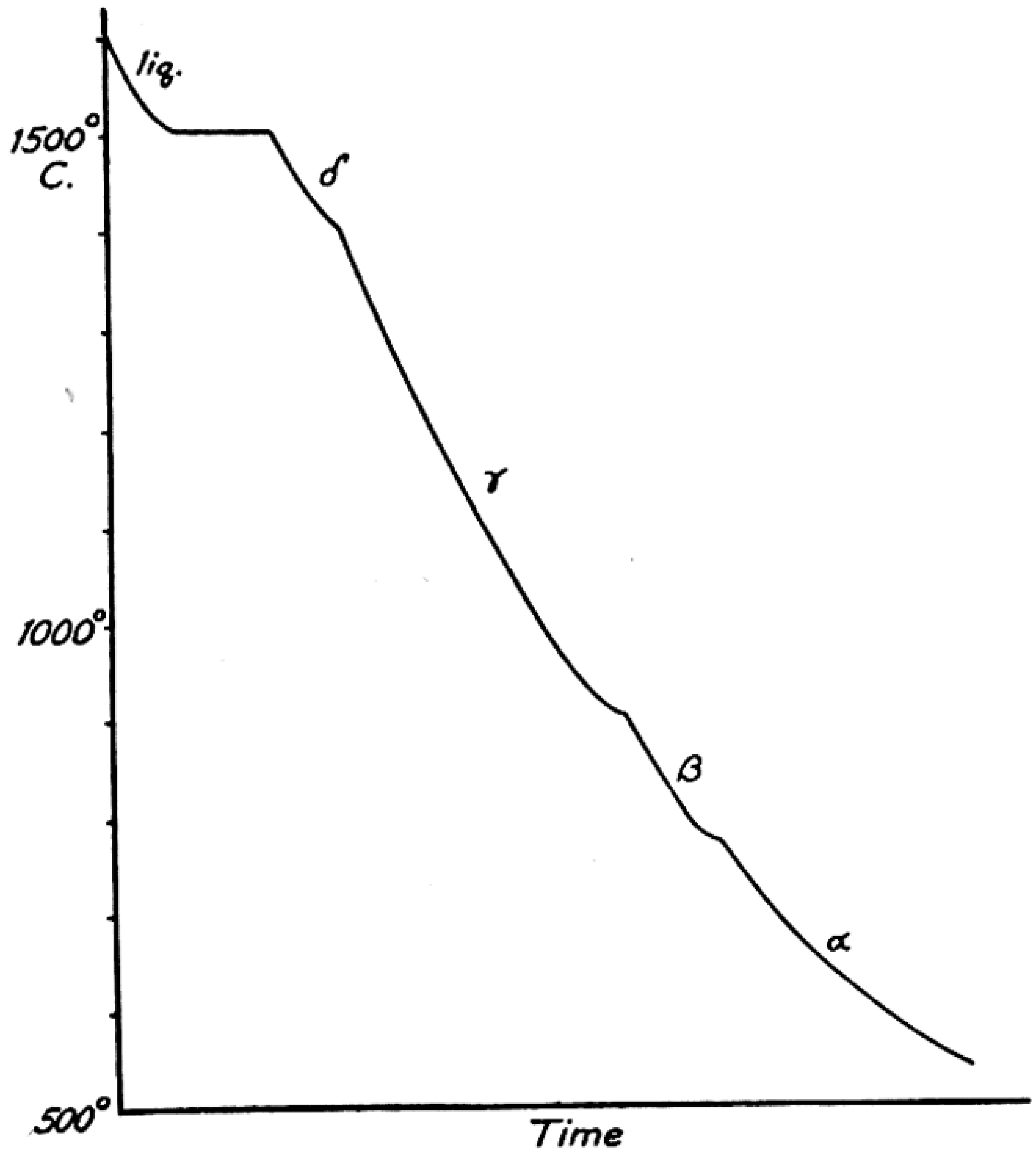

FIG. 83. Cooling curve for pure iron, showing transition temperatures.

Transition Temperatures: Experimental. By plotting the cooling curve of a specimen the transition temperatures may be observed as shown in Fig. 83. If the cooling is too rapid, however, the transition point may be unnoticed. To emphasize the discontinuity it is often advantageous to employ a differential method. A neutral sample is placed in good thermal contact with the specimen and both bodies are allowed to cool together. One junction of a thermocouple is placed in a drill hole in the test specimen and the other junction is electrically insulated and placed in a drill hole in the neutral body. The thermocouple is connected to a galvanometer whose deflection is observed. On passing through the transition point the specimen lags in its rate of cooling and a substantial deflection occurs.

For those substances for which a change in magnetic permeability accompanies the transition from one phase to another, other methods may be employed. In Fig. 84 the specimen is made a part of the magnetic circuit of a transformer. By observing the electromotive force set up in the secondary by a definite alternating current in the primary, any change in the reluctance due to heating the specimen may be noted. At the transition temperature an abrupt change may be expected.

A measurement of the high-frequency resistance of the specimen may be used to detect the transition temperature. An arrangement of this sort making use of the method of substitution is shown in Fig. 85. The results obtained[2] by Bryant and Webb on an alloy of iron, nickel, and chromium are summarized in Fig. 86. The high-frequency resistance is dependent upon the depth of penetration of the current

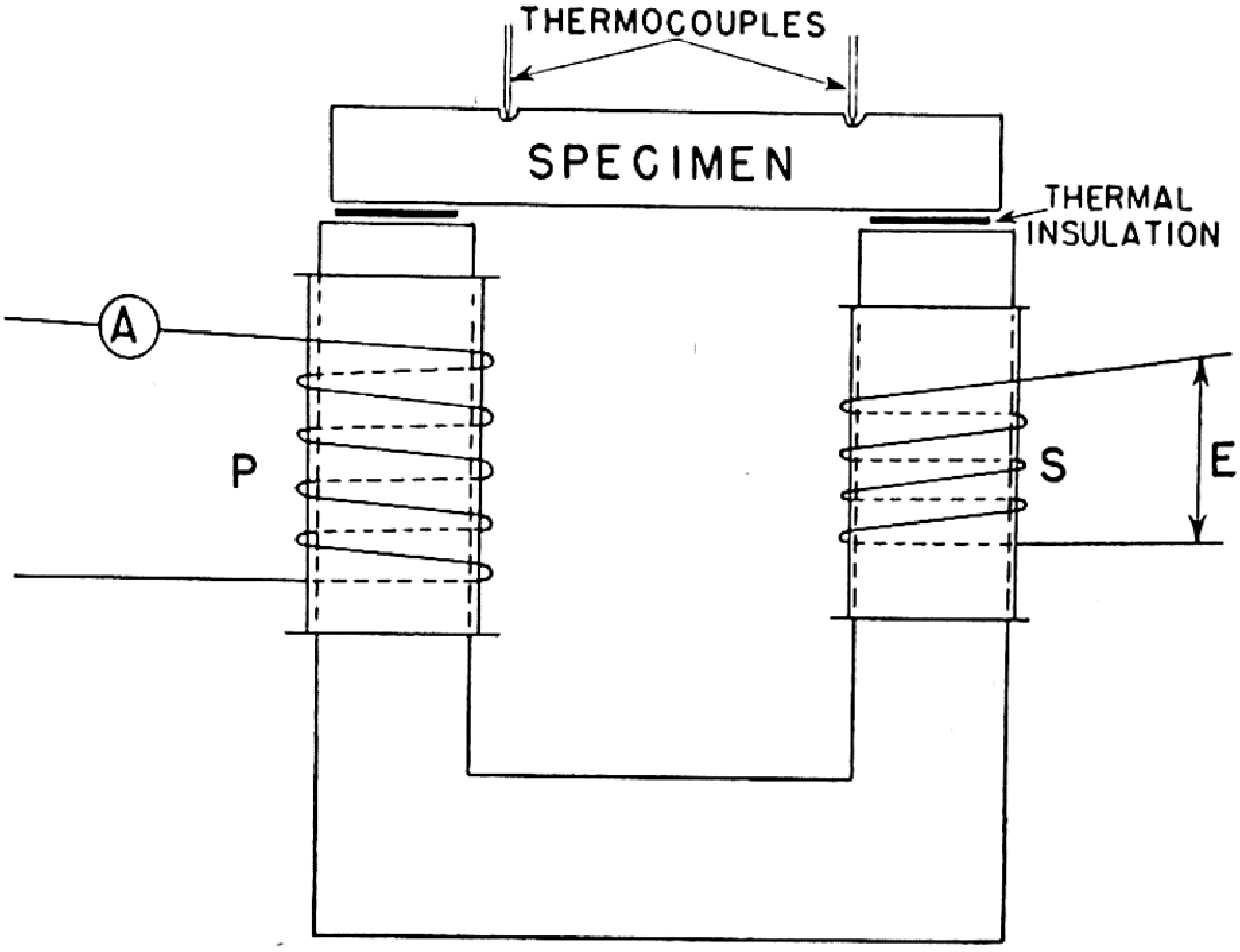

FIG. 84. Apparatus to observe transition points by observing the change in magnetic reluctance.

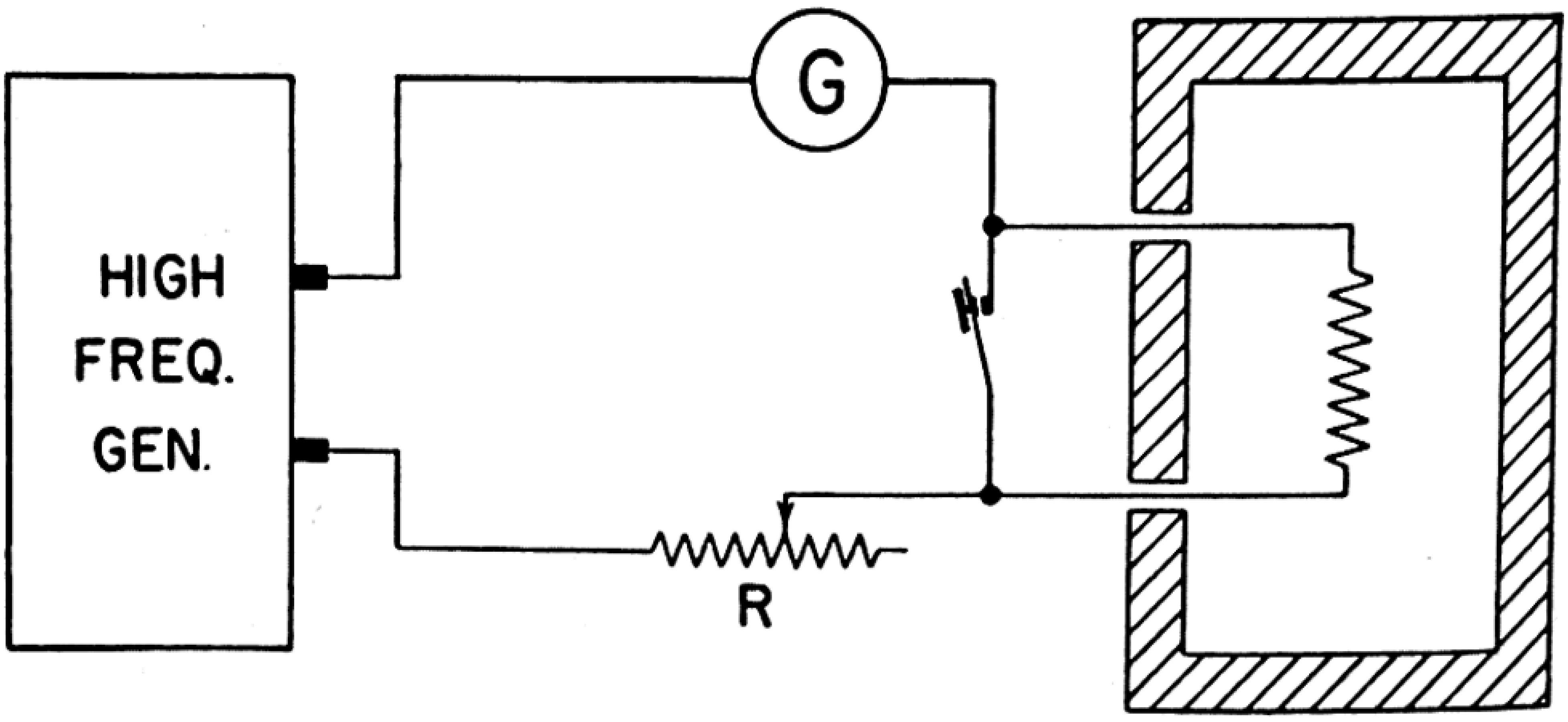

FIG. 85. Apparatus to determine transition points by the method of high-frequency resistance.

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[2] J. M. Bryant and J. S. Webb, *Rev. Sci. Inst.*, **10**, 47 (1939).

into the conductor, which in turn depends upon the permeability of the material. This changes abruptly at the transition temperature.

Heat of Fusion. The latent heat of fusion of a substance has already been defined as the quantity of heat liberated when one gram of liquid is converted into a solid with no change in temperature. By multiplying this quantity by the atomic weight or the molecular weight of the substance, the atomic or molecular heats of fusion are obtained.

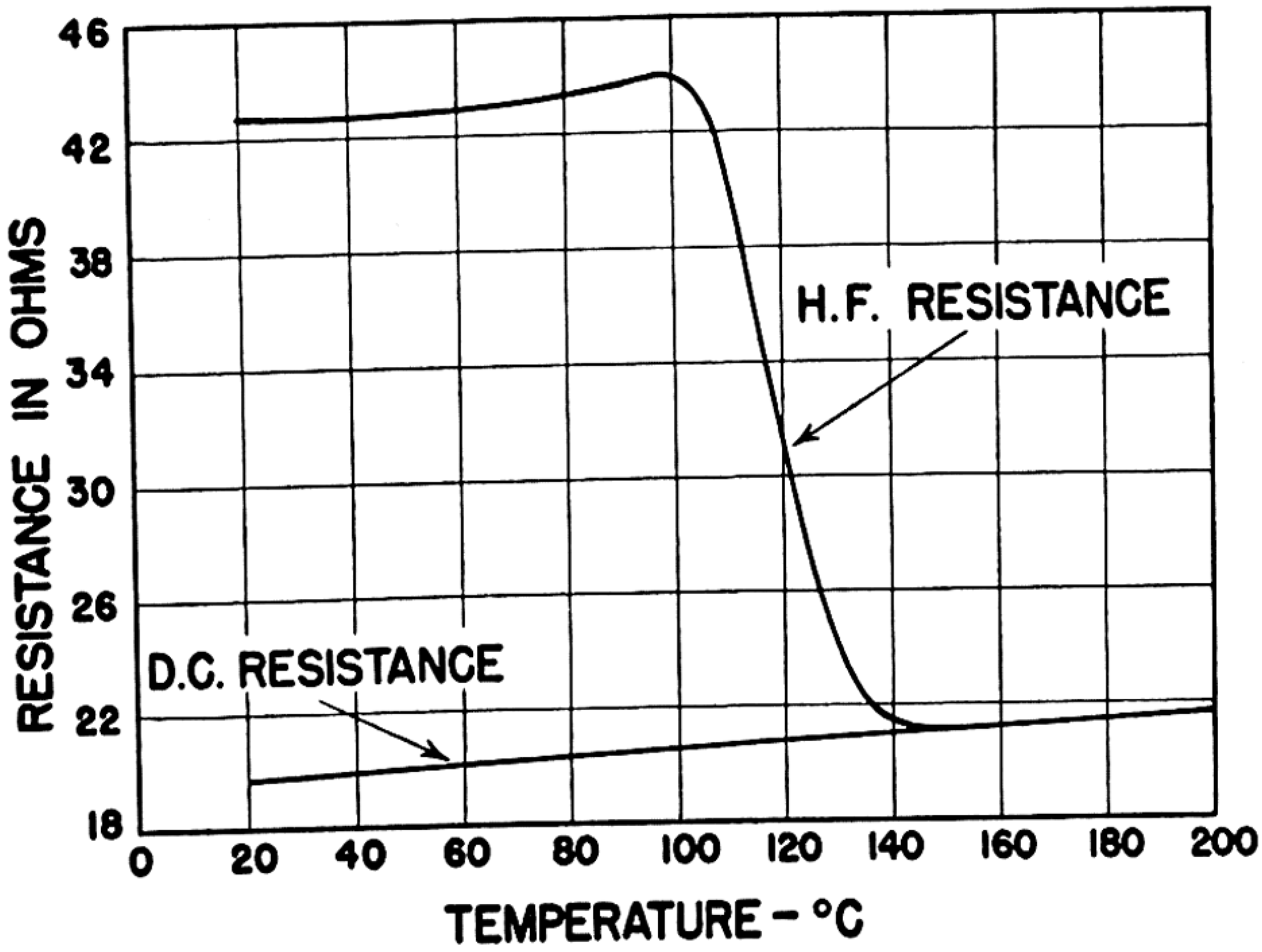

FIG. 86. The variation in high-frequency resistance with temperature.

From classical theory a comparison of the specific heat of the liquid phase and that of the solid phase of a substance at the freezing point allows a determination of the number of new degrees of freedom springing into existence upon melting. As shown in equation 62, in Chapter II

$$C_L - C_S = \Delta f \cdot \frac{R}{2} \qquad (1)$$

where C_L and C_S are the atomic heats of liquid and solid respectively, Δf is the increase in the number of degrees of freedom, and R is the universal gas constant. Now allowing $\frac{1}{2}RT$ for the energy of each degree of freedom created, the expected value for the latent heat per gram-atom is at once obtained. This value as computed is in general too small, since it takes no account of the change in volume occurring during fusion. For water the calculated value would be too large since the specific volume of the liquid is smaller than that of the solid at the melting point.

Experimental methods that may be employed to determine the heat of fusion are identical with those methods applicable to the determination of the specific heat of a substance and already described. The method of mixtures has been used by E. Griffiths and Awbery[3] in a systematic study of the latent heat of fusion of the common metals.

For the common metallic elements a rather striking approximate relationship is found to hold between the atomic heat of fusion and the melting temperature. This may be stated as follows: The atomic latent heat of fusion divided by the melting temperature on the absolute scale for the common metals equals a constant, namely, 2.4. For substances differing as widely as mercury and silver the agreement is satisfactory. For compounds the ratio has a larger value.

Vaporization. When a particle finds itself at the free surface of a liquid, with a velocity directed out from the surface, it will be acted upon by an attractive force tending to draw it back into the liquid. This backward force will, of course, diminish, the farther the particle is able to get away from the surface. If the initial velocity has a normal component greater than a certain critical value, the particle will be able to get away completely and become a gas particle. Reference to Fig. 24 shows that at any temperature there are always some particles with velocities greater than any particular critical value. This process in which the particles with higher velocities are continuously leaving the liquid (or solid) is termed evaporation. Figure 24 shows that at a higher temperature more particles would possess velocities above any particular critical value, or that evaporation would take place more rapidly. At a sufficiently high temperature, vapor is able to form throughout the body of the liquid, and it then is said to boil.

The particles which get away are on the average those of greatest kinetic energy. The average kinetic energy of those particles that remain is therefore continually lessened, unless heat is added from an outside source. This means that the temperature of the remaining liquid is reduced by the evaporation from the surface.

The temperature at which the substance boils is influenced by the presence of impurities, as might be expected. Impurities in general act to raise the boiling temperature of a substance. For small amounts of impurities the elevation in the boiling point of the mixture is proportional to the quantity of foreign substance present.

Vapor Pressure. Let it be imagined that a liquid is suddenly exposed in an evacuated chamber provided with a device for observing any pressure that might be developed in the enclosure. An abrupt increase in pressure p will be observed, as shown in curve A, Fig. 87. If the enclosure already possessed an initial pressure P_0 due to other gases being present, then an increase in pressure p will be observed as before, except that now it will require a long time to attain the maximum value of the pressure as shown in curve B, Fig. 87. This value p is termed the saturated vapor pressure, or vapor tension of the liquid at the particular temperature employed. If this experiment is repeated at various temperatures, data may be obtained for plotting a vapor tension curve as shown in the upper part of Fig. 88. This curve does not extend indefinitely in either direction but has definite terminals. The upper extremity is termed the critical point. At temperatures greater than the critical temperature the gas cannot be liquefied by the application of pressure. The curve is often called a boiling-point curve, since a liquid will boil at any temperature along the curve if the total pressure to which it is subjected is less than its vapor tension at that temperature.

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[3] J. H. Awbery and E. Griffiths, *Proc. Phys. Soc.* (*London*), **38**, 378 (1926).

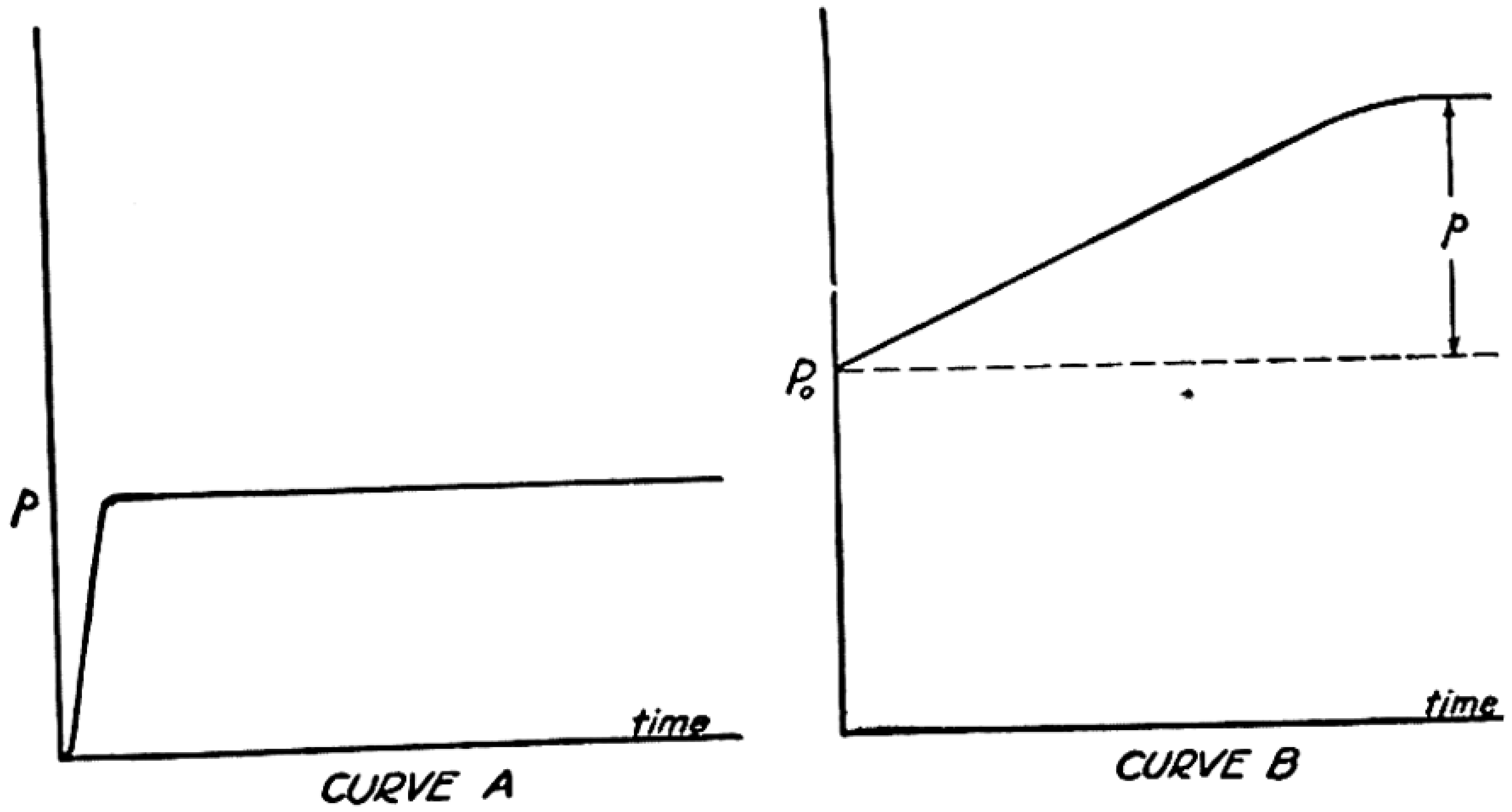

FIG. 87. Vapor pressure and the time required for saturation.

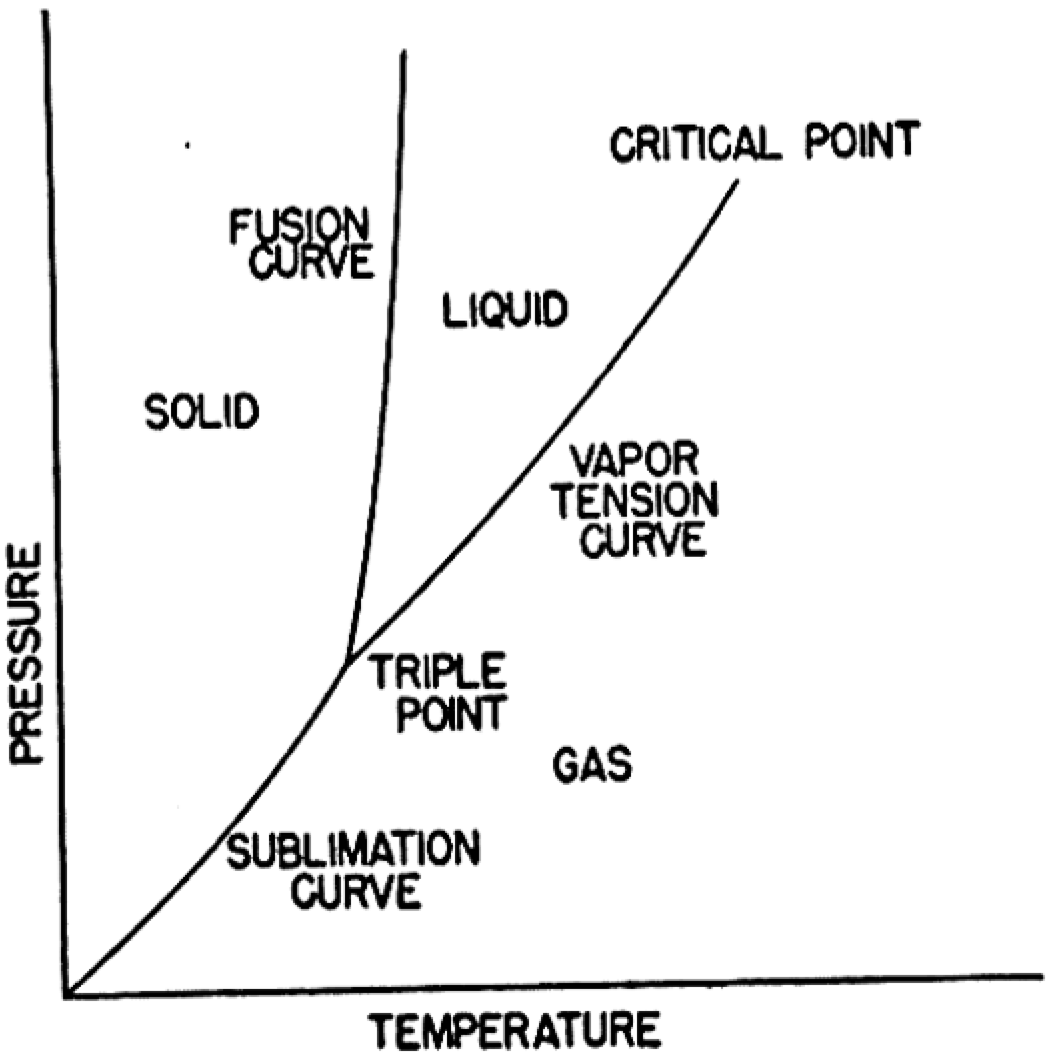

FIG. 88. Equilibrium diagram on a pressure-temperature plot.

A similar consideration applies to the vapor tension of a solid substance. In this case a curve is obtained as shown in the lower part of

Fig. 88, called the sublimation or frost curve. These curves meet at the triple point, at which position the gas, liquid, and solid may exist in equilibrium. That the slope of the sublimation curve is greater than that of the vapor tension curve at the triple point will be shown from thermodynamic considerations, page 241. The sublimation pressure might be expected to be zero in value at the absolute zero of temperature. This is not necessarily true. Certain experiments[4] indicate that there is a "zero-point" energy, that is, that at the absolute zero of temperature the particles are not entirely without motion. Hence there would be also a "zero-point" pressure.

Experimental Methods — Vapor Pressure. *Static Method.* Perhaps the most straightforward method to determine vapor pressure experimentally is illustrated by the apparatus shown in Fig. 89. The applicability of the apparatus is determined by the properties of the substance under investigation. Vapor pressures under a few millimeters in value cannot be measured with accuracy, but large values are readily observed. The substance S at the temperature T exerts the measurable pressure $(B - A) + P_0$. P_0 may be zero or atmospheric pressure or a pressure of several atmospheres. For high pressures, the chamber at the left is filled with a gas such as nitrogen at a pressure of several atmospheres and sealed at C. As the temperature of S is increased, the increase in the vapor tension forces mercury over into the left tube, compressing the nitrogen. Since the nitrogen obeys Boyle's law, the observed decrease in the volume makes it possible to compute the new pressure. The level A is generally maintained in the same position during the complete experiment by the adjustment of the communicating reservoir of mercury. At high temperatures the partial pressure of the mercury vapor becomes appreciable, and since it is present in S together

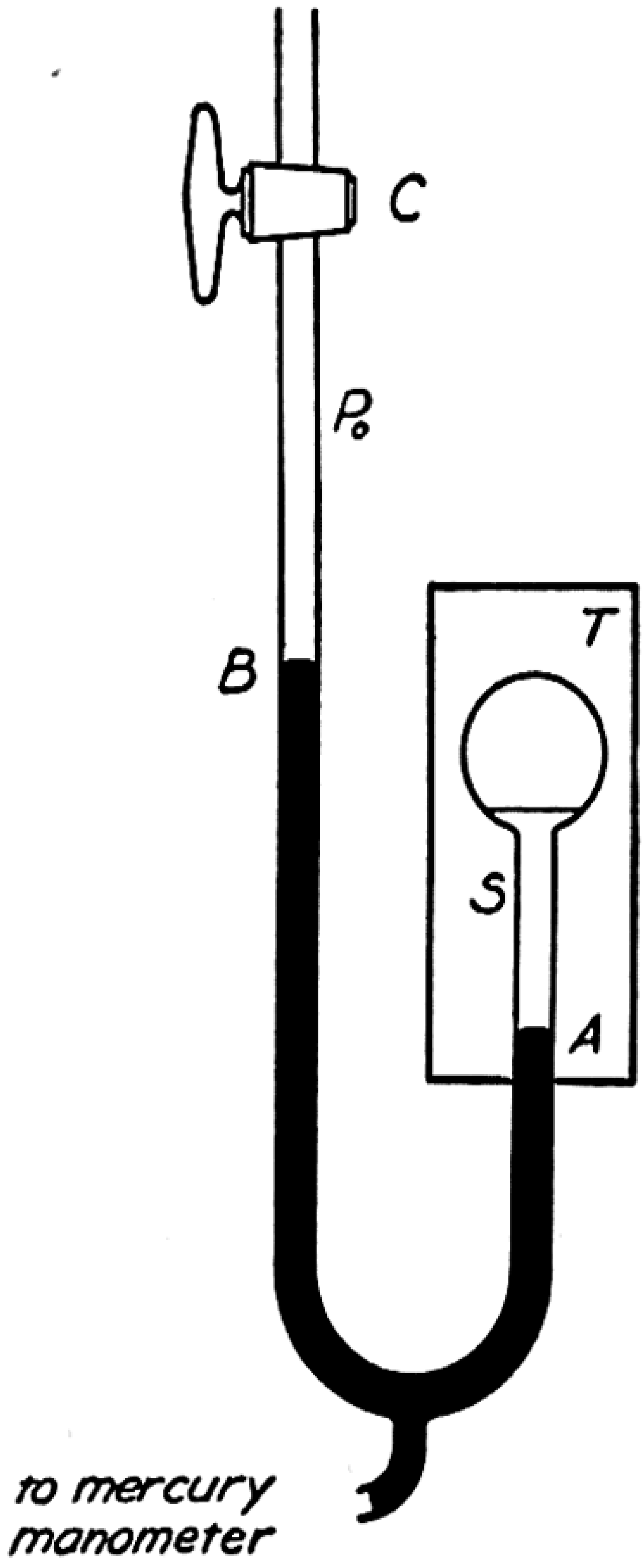

FIG. 89. Apparatus to determine vapor tension by the static method.

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[4] See, for example, A. Einstein and W. J. de Haas, *Verh. deut. phys. Ges.*, **17**, 152 (1915); E. Beck, *Ann. Physik.*, **60**, 109 (1919); R. W. James and G. W. Brindley, *Proc. Roy. Soc.*, **121**, 155 (1928).

with the vapor under investigation it must be subtracted from the total measured pressure.

Boiling-Point Method. It has been pointed out that the vapor tension-temperature curve may be termed a "boiling-point" curve, since a substance will boil if the pressure to which it is subjected is made infinitesimally less than the vapor tension at that temperature. Thus the substance under examination may be placed in a boiler, communicating through a condenser to a chamber provided with a manometer or gage as shown in Fig. 90.

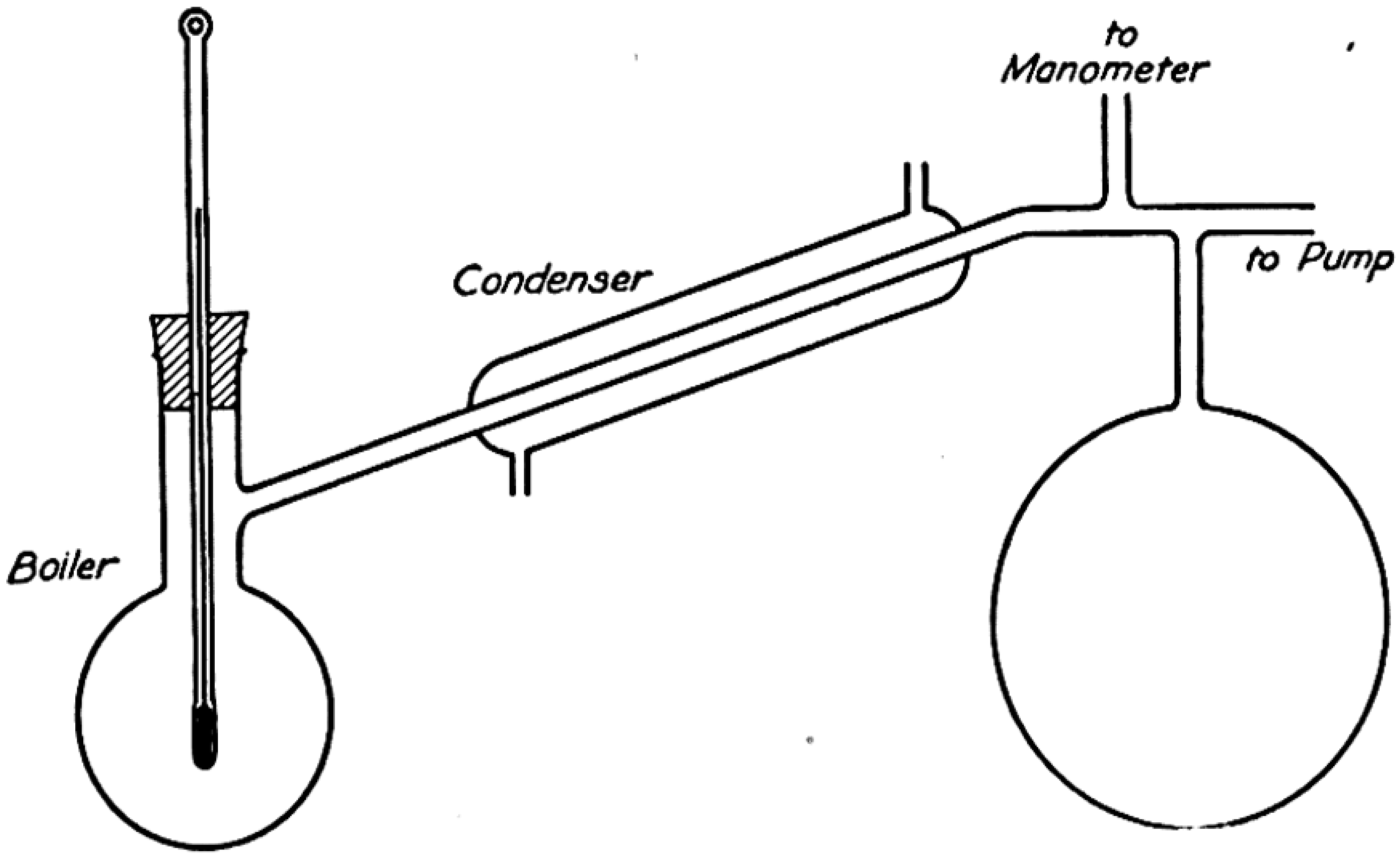

FIG. 90. Apparatus to determine vapor tension by the boiling-point method.

Above the boiling liquid is placed a thermometer or the hot junction of a calibrated thermocouple for indicating the temperature. By means of a vacuum pump or compressor the pressure may be adjusted to any desired value and the boiling temperature observed. These values of the vapor tensions and the corresponding temperatures when plotted on a suitable coordinate system give the vapor-tension curve.

Vapor Pressure from the Rate of Evaporation — Langmuir. In the technique of obtaining high vacua it is apparent that no substance with a high vapor tension at the temperature used may be exposed to the evacuated enclosure. Thus in a sealed x-ray tube a pressure as great as one ten-thousandth of a millimeter of mercury would be undesirable. It is thus important to know the vapor tension of materials even though they are very small. A method in which the vapor tension of a solid is determined by observing the rate at which it evaporates in a vacuum has been described by Langmuir.[5] When a liquid or solid is in equilibrium with its own vapor, the number of particles per square centimeter per second leaving and entering the substance are identical. From the universal gas law ($PV = RT$) the density of the vapor ρ_v may be found. Since the density is the reciprocal of the specific volume V, then

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[5] I. Langmuir, *Phys. Rev.*, **2**, 329 (1913); I. Langmuir and G. M. J. Mackay, *Phys. Rev.*, **4**, 377 (1914).

$$\rho_v = \frac{P(\text{M.W.})}{RT} \tag{2}$$

where (M.W.) represents the molecular weight of the substance, P and T are its pressure and absolute temperature respectively, and R is the universal gas constant. From kinetic theory, for a Maxwellian distribution of velocities the average velocity $\overline{V}$ at the temperature T is

$$\overline{V} = \sqrt{\frac{8RT}{\pi(\text{M.W.})}} \tag{3}$$

Now from a consideration similar to that used in developing equation 28, in Chapter V for radiation, the mass of material (m) received per square centimeter per second is

$$m = \tfrac{1}{4}\rho_v\overline{V} = P\sqrt{\frac{(\text{M.W.})}{2\pi RT}} \tag{4}$$

In the condition of equilibrium this is also the mass of material leaving the surface per square centimeter per second. If the vaporizing surface be exposed to a vacuum this still represents the rate at which mass is lost. Now for a heated cylindrical wire of radius r the mass loss per unit length per second m_l is

$$m_l = 2\pi r \cdot m = 2\pi r P\sqrt{\frac{(\text{M.W.})}{2\pi RT}} = \rho_s\frac{d(\pi r^2)}{dt} \tag{5}$$

in which ρ_s denotes the density of the solid substance.

The quantity m_l may be experimentally evaluated by weighing the wire at the beginning and end of an interval of time t. Let these masses be called M_1 and M_2 respectively. During this time the wire is maintained at the constant temperature T, as measured by an optical pyrometer.

The definite integration of the last two terms of equation 5 using the limits that, at $t = 0$, $r = r_1$, and $r = r_2$ at $t = t$, gives

$$P \cdot t\sqrt{\frac{(\text{M.W.})}{2\pi RT}} = \rho_s(r_1 - r_2) = \frac{\sqrt{\rho_s M_1} - \sqrt{\rho_s M_2}}{\sqrt{\pi}} \tag{6}$$

This leads to the desired expression for the pressure:

$$P = \frac{\sqrt{2RT\rho_s}[\sqrt{M_1} - \sqrt{M_2}]}{t\sqrt{(\text{M.W.})}} \tag{7}$$

A somewhat modified form of this method, making use of the rate of diffusion of the vapor through a small opening, was proposed by Knudsen.[6] This method is particularly applicable to the measurement of very low vapor pressures, and has been used by Egerton[7] on zinc, cadmium, and lead at low temperatures.

Vapor Pressure and Temperature. No satisfactory theoretical expression has been derived to relate the variation in the vapor pressure of a particular substance with temperature. Such a relationship might follow from a consideration of the rate at which an increase in temperature increases the number of particles, with velocities above a limiting critical value, as shown in Fig. 24. The equation of the curve for the Maxwellian distribution of velocities (page 46) suggests a logarithmic relationship such as

$$P = C_1 e^{-C_2/T} \tag{8}$$

where P is the pressure of the saturated vapor, C_1 a constant, e the base of the Naperian system of logarithms, T the absolute temperature of the liquid, and C_2 is a constant related to the average kinetic energy of the particles of the liquid. This relationship may be written as follows:

$$\log P = A + \frac{B}{T} \tag{9}$$

where A and B are constants. Indeed, equations as simple as this are found to represent satisfactorily the results for many substances, both liquids and solids. This is shown by plotting the log P against $1/T$ and noting the constancy of the slope of the resultant curve. A more exact empirical representation is, of course, given by introducing additional constants. The following equations have been proposed and found to be very satisfactory in representing the variation in the vapor pressure of certain substances:

Rankine:[8]

$$\log P = A - \frac{B}{T} - \frac{C}{T^2} \tag{10}$$

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[6] M. Knudsen, *Ann. Physik.*, **29**, 179 (1909).

[7] A. Egerton, *Proc. Roy. Soc.*, **113**, 520 (1927).

[8] W. J. M. Rankine, *Phil. Mag.*, **8**, 530 (1854).

Kirchhoff:[9]

$$\log P = A - \frac{B}{T} - C \log T \tag{11}$$

In each, A, B, and C are empirical constants. Although the equation of Kirchhoff was proposed merely as a satisfactory empirical relationship it will be shown (see page 203) to follow from certain thermodynamic considerations.

Latent Heat of Vaporization. When unit mass of a liquid or of a solid is transformed into a vapor with no change in temperature, a definite quantity of heat, known as the latent heat of vaporization or latent heat of sublimation, is required. The various experimental methods employed in the determination of specific heats are all applicable to the measurement of latent heats. Many classical experiments having to do with the latent heat of water and other substances at various temperatures have been carried out. Among these may be mentioned the work of Berthelot,[10] using the condensation method; Henning[11] employing an electric method; Smith,[12] an electrical method; and Awbery and Griffiths,[13] using a continuous-flow condensation method.

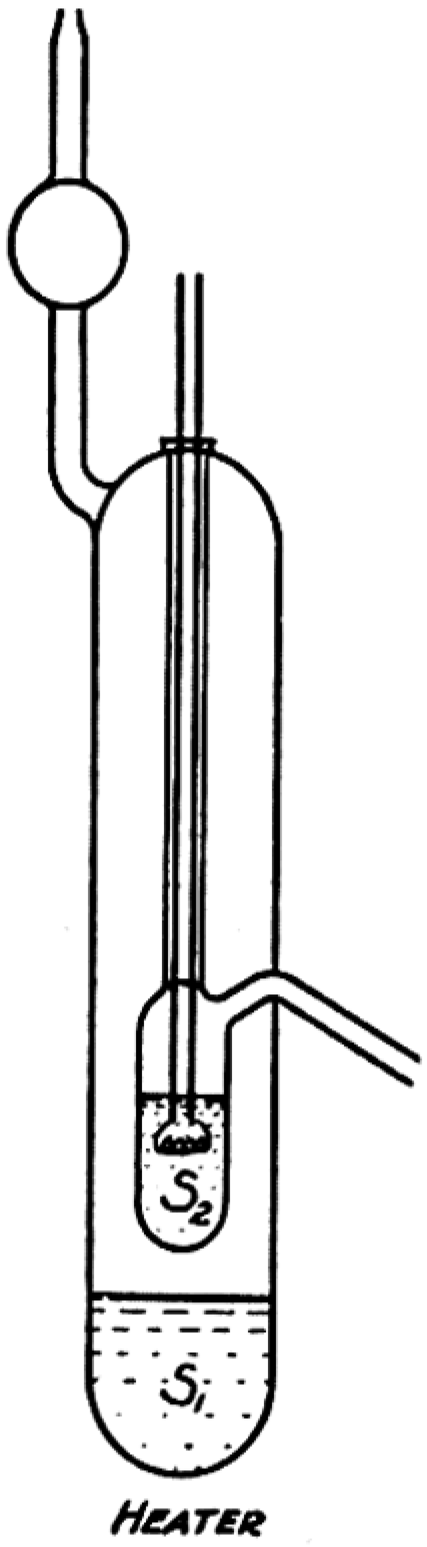

FIG. 91. Apparatus to determine the heat of vaporization.

An apparatus suitable for the determination of the latent heat of vaporization of a substance with considerable accuracy is shown in Fig. 91. The material under investigation is placed in the tubes S_1 and S_2. Power is supplied to an outer heating coil until the whole system attains the equilibrium temperature characteristic of the boiling point of the substance. Electric power at a definite known value EI is now supplied to S_2, driving over vapor at a uniform rate. The mass of liquid m_L evaporated in the time t is condensed and weighed. When the apparatus is properly manipulated, losses of heat by radiation are thus entirely avoided and the expression for equivalent energies follows:

$$\frac{EIt}{J} = m_L L_V \tag{12}$$

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[9] G. Kirchhoff, *Pogg. Ann.*, **103**, 185 (1858).

[10] D. Berthelot, *Jour. Phys.*, **6**, 337 (1877).

[11] F. Henning, *Ann. Physik.*, **21**, 849 (1906); **58**, 759 (1919).

[12] A. W. Smith, *Phys. Rev.*, **33**, 173 (1911).

[13] J. H. Awbery and E. Griffiths, *Proc. Roy. Soc.*, **36**, 305 (1924).

By introducing the mechanical equivalent of heat J, the heat of vaporization L_V may be expressed in calories per gram.

Latent Heat of Vaporization of Water. The results of various investigators for the latent heat of vaporization of water vary in value from about 536 cal. per gm. to 540.4 cal. per gm. Aside from losses due to radiation, there are two possibilities for error in the investigation. One of these, leading to a value for L_V too high, is due to superheating the vapor. The other source of error, leading to too small a value for L_V, is due to the fact that, in rapid boiling, small particles of liquid (mist) may be carried along with the vapor. Since the molecules of such liquid particles are not separated, mass is contributed to the condensed vapor without a corresponding absorption of heat from the source of power. In the investigation of Smith a current of air heated to the temperature of the evaporating liquid was directed against the quiet surface of the liquid. In this way it was estimated that no mist particles existed in the vapor. In this experiment the highest value for L, namely, 540.4 cal. per gm., was obtained. This value agrees satisfactorily with a value calculated from other physical constants by the Clausius-Clapeyron equation (see page 240). This calculation gives

$$L_V = T(V_V - V_L)\left(\frac{\partial P}{\partial T}\right)_{100} = 541.2 \text{ cal. per gm.} \qquad (13)$$

T is the absolute temperature at which vaporization occurs, V_V and V_L are the specific volumes of saturated vapor and liquid, respectively, and $\partial P/\partial T$ is the rate of variation of the vapor tension of the substance with temperature at the boiling point. Such calculations, however, are subject to errors sufficiently large to render them invalid in discriminating in favor of a particular investigation. The latent heats of a few common materials are tabulated, together with the transition temperatures in Table 11.

Variation of Latent Heat of Vaporization with Temperature. The latent heat of vaporization L_V of a substance varies with the temperature at which it is observed. In general, the higher the temperature, the less is the value of the latent heat. At the critical temperature the vapor and liquid states are indistinguishable, and consequently at that temperature the latent heat is zero. For most substances the specific heat of the vapor phase is less than that of the liquid phase over the same range in temperature. This fact may be regarded as an explanation of the observed variation of L_V with T. To demonstrate the relationship, imagine a gram molecular weight of a liquid at a temperature T_1 to be transformed into a vapor at some higher temperature

TABLE 11

THE HEAT OF VAPORIZATION OF SOME COMMON SUBSTANCES

Substance		$L \frac{\text{cal.}}{\text{gm.}}$	Temperature
Name	Symbol		
Air	$N_2 + O_2$	49.3	−188° C.
Mercury	Hg	67.9	357
Carbon dioxide	CO_2	79.6	− 40
		137.5	− 78.5
Sulphur dioxide	SO_2	95.0	− 10.1
		115.6	− 40
Ammonia	NH_3	327	− 33.4
		332	− 40.0
Water	H_2O	539.5	100

T_2. This process may be accomplished by first raising the temperature of the liquid from T_1 to T_2 and then vaporizing, or the liquid may be vaporized at T_1 and then the vapor heated under the condition of constant volume to T_2. In each case the change in the internal energy (see Joule's law, page 227) must be the same. If $(\text{S.H.})_L$ denotes the specific heat of the liquid and $(\text{S.H.})_V$ and $(\text{S.H.})_V^V$ are respectively the specific heat of the vapor under the condition of constant pressure and that under constant volume, and if the small amount of external work during the heating of the liquid be neglected, then:

$$\int_{T_1}^{T_2} (\text{S.H.})_L dT + (L_V)_{T_2} - P_2(V_V - V_L)_2$$

$$= (L_V)_{T_1} + \int_{T_1}^{T_2} (\text{S.H.})_V^V dT - P_1(V_V - V_L)_1 \qquad (14)$$

Now if the relatively small volumes of the liquid V_L be rejected in comparison with the much larger volumes of vapor V_V and if the vapor be treated as an ideal gas, so that $P_2V_2 = RT_2$ and $P_1V_1 = RT_1$ and $(\text{S.H.})_V - R$ be written for $(\text{S.H.})_V^V$ then it follows that

$$(L_V)_{T_1} = (L_V)_{T_2} + \int_{T_1}^{T_2} [(\text{S.H.})_L - (\text{S.H.})_V]dT \qquad (15)$$

Regnault investigated the behavior of water with respect to the effect upon L_V of a change in temperature. His conclusion expressed empirically in terms of the centigrade temperature gave the value of the latent heat of vaporization as

$$L_T = 606.5 - 0.695T - 0.00002T^2 - 0.0000003T^3 \cdots \qquad (16)$$

More recent measurements indicate that corrections to this expression are necessary, but as mentioned on page 201, agreement between the experimental values of different observers is not good even at the normal boiling point.

Vapor Pressure and the Chemical Constant. Equation 11 for vapor pressure, as proposed by Kirchhoff may now be shown to follow from equation 13 if the following approximations are made: (*a*) The volume of the liquid V_L may be neglected in comparison with the much larger volume of the vapor V_V. (*b*) The vapor obeys the law for ideal gases, so that V_V may be replaced by RT/P. (*c*) The latent heat of vaporization L_T at any temperature T may be expressed in terms of the latent heat at 0° C. by equation 15 where the specific heats are regarded as constants. Then by substitution in equation 13 and separating the variables the following expression is obtained:

$$\frac{dP}{P} = \frac{L_0}{R} \cdot \frac{dT}{T^2} + \frac{1}{R}\left[(\text{S.H.})_V - (\text{S.H.})_L\right]\frac{dT}{T} \tag{17}$$

The integration of equation 17 gives

$$\log P = -\frac{L_0}{RT} + \frac{1}{R}[(\text{S.H.})_V - (\text{S.H.})_L] \log T + i \tag{18}$$

Nernst[14] has called attention to the importance to be attached to the constant of integration i which is introduced here. This quantity is called the chemical constant and has a characteristic value for every vapor. Sackur[15] has shown that, for any vapor, i may be expressed as:

$$i = \log_e \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \tag{19}$$

where k is the Boltzmann gas constant, h is the Planck constant, and m is the mass of an individual molecule of the vapor.

Trouton's Law Regarding Vaporization. An empirical rule regarding the latent heat of vaporization of substances and their boiling temperatures was observed by Trouton.[16] This principle may be stated as follows: The ratio of the latent heat of vaporization per gram-mole of any substance to its normal boiling temperature T_b on the absolute scale is equal to a constant, the constant being the same for all substances. The extent to which the rule holds for a few substances is shown in Table 12. For the last six elements the average value is 21.4. Neglecting hydrogen, the other substances agree with this value within 20 per cent. This is noteworthy, since the individual quantities T_b and L_V vary by factors as great as twenty. Many attempts to improve upon this empirical relationship by substituting others of a less simple nature have been proposed.[17]

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[14] See W. Nernst, *The New Heat Theorem*, p. 166, *et seq.*, 1926.

[15] O. Sackur, *Ann. Physik*, **40**, 67 (1913).

[16] F. T. Trouton, *Phil. Mag.*, **18**, 54 (1884).

TABLE 12

THE RATIO BETWEEN THE HEAT OF VAPORIZATION AND THE BOILING POINT

Substance	Heat of Vaporization L_V (gm-mol.)	Normal Boiling Point T_b	Trouton's Constant L_V/T_b
H_2	219 cal.	20.4° A.	10.8
N_2	1 340	77.3	17.3
O_2	1 630	90.1	18.1
Cl_2	3 600	239.5	19.2
H_2O	9 710	373	26.0
Hg	14 200	630	22.6
Cs	15 600	858	18.2
Rb	18 700	942	19.9
Na	23 300	1 155	20.2
Zn	27 730	1 180	23.5
Pb	46 000	1 887	24.4

Hygrometry — Humidity. The values of the sublimation pressure and the saturated vapor pressure of water at various temperatures are important in their application to meteorology. Relative humidity, by which is meant the ratio between the mass of water vapor per cubic centimeter to the mass per cubic centimeter if the vapor were saturated at that temperature, may be readily obtained. If the existing vapor pressure at the temperature T is some value as represented by the point a in Fig. 92, then a sufficient reduction of temperature to T_d will render the vapor in the saturated condition b. This temperature is called the dew-point and may be readily observed by various so-called "dew-point devices." In some of these a polished surface is observed as it is progressively cooled by being in thermal contact with an evap-

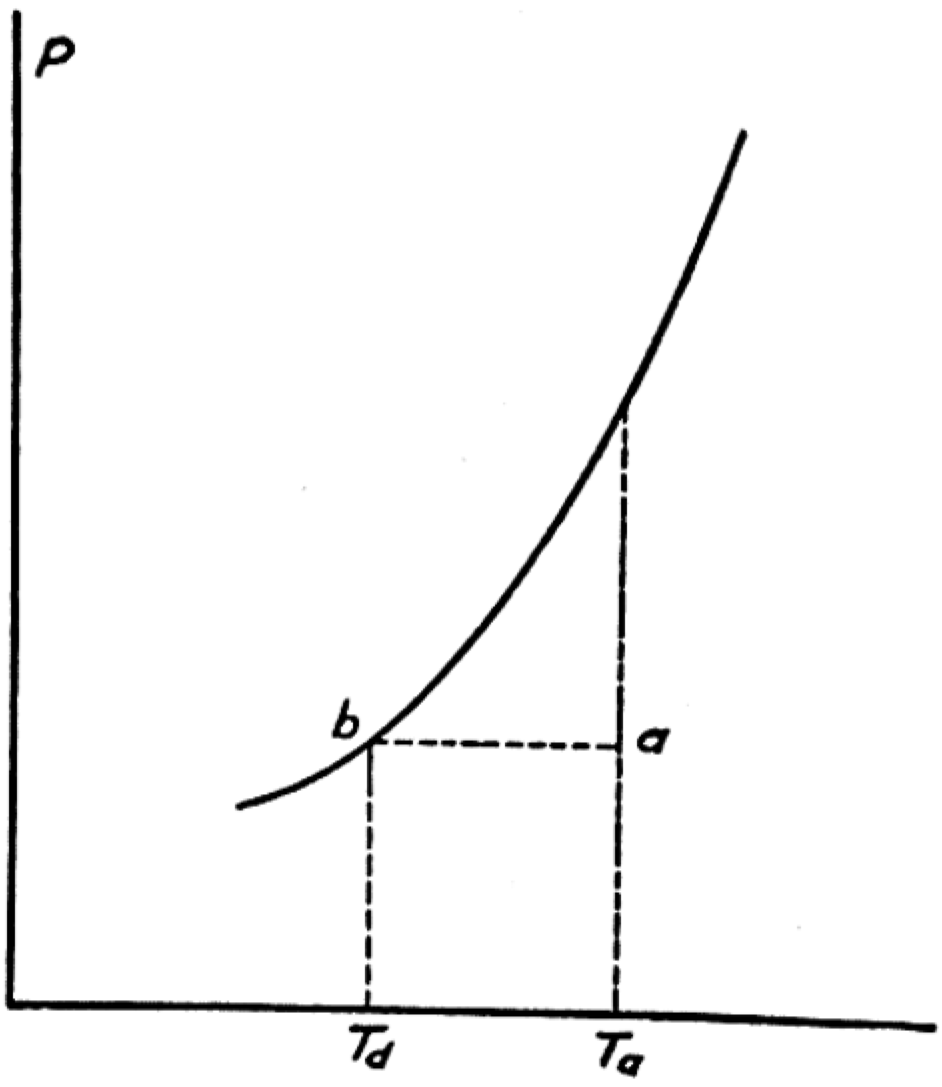

FIG. 92. Vapor-tension curve and the dew-point.

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[17] H. von Wartenburg, *Zeit. Electrochem.*, **20**, 444 (1914); C. Wagner, *Zeit. Electrochem.*, **31**, 308 (1925).

orating liquid such as ether. The temperature is observed at the instant droplets of dew or frost begin to form. The ratio of the ordinate of the vapor-tension curve at this temperature T_d to the ordinate at T_a expresses the relative humidity.

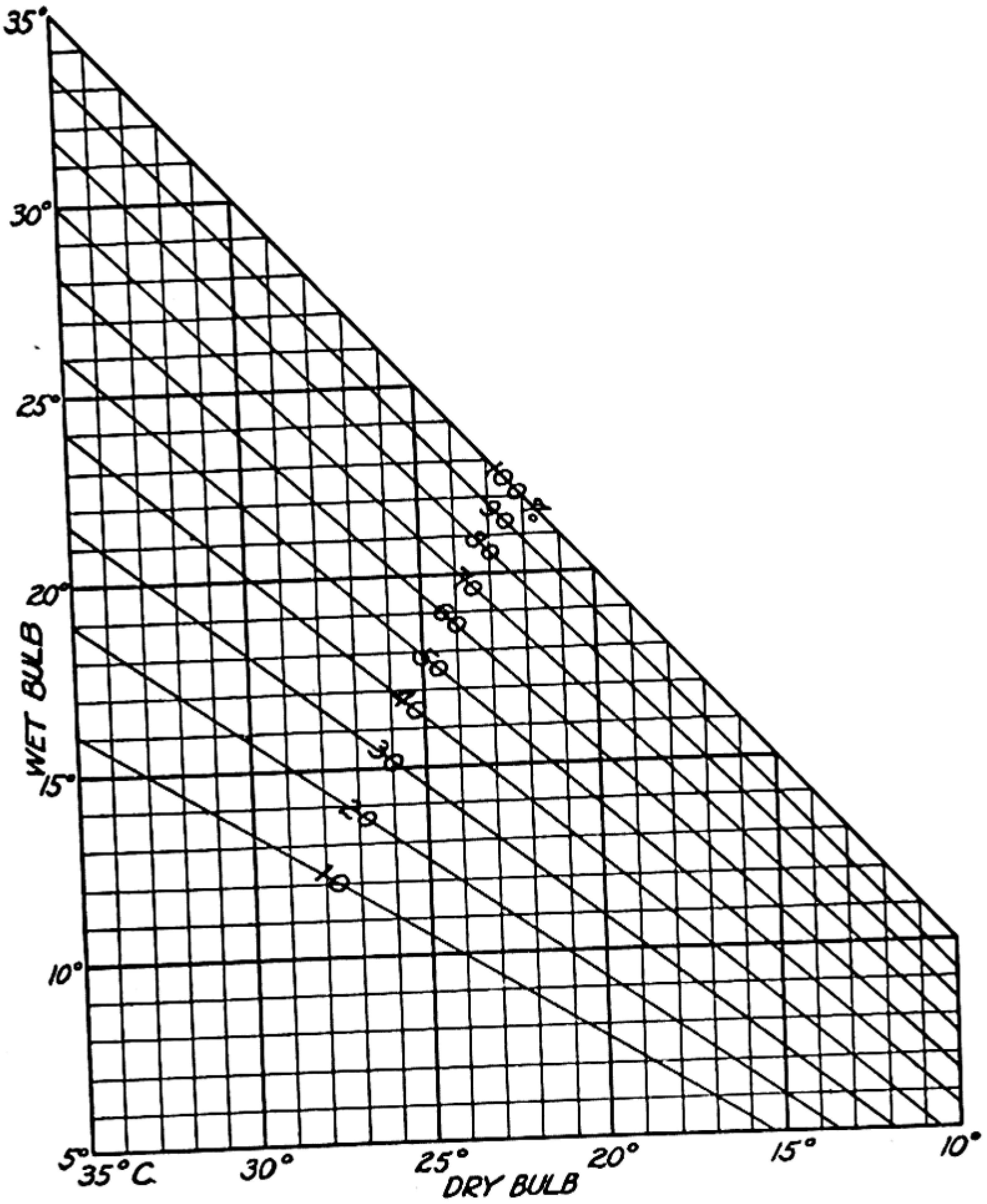

FIG. 93. Relative humidity from the readings of wet and dry bulb thermometers.

Many other devices may be calibrated empirically so as to give relative humidity directly. Certain animal fibers alter their length with any change in the humidity, and they may be made to actuate a pointer moving over a scale graduated to read relative humidity.

A current of air passing over two adjacent thermometer bulbs, one of which is surrounded by evaporating water, produces a difference in the readings of the two thermometers. The magnitude of this difference is dependent upon the relative humidity. For forced ventilation at a definite rate it is possible to determine the relative humidity directly from the readings of the two thermometers. Figure 93 is an empirical chart from which this result may be found. The reading of the thermometer with the dry bulb is laid off along the horizontal scale.

Along the vertical scale is marked the reading of the thermometer with the wet bulb. From the position of the point whose coordinates are these two values, the relative humidity may be interpolated.

Cooling by Evaporation. The transformation of a liquid into a vapor is accompanied by the absorption of an amount of heat dependent upon the heat of vaporization at the transformation temperature. If this process of evaporation is made to proceed continuously by removing the vapor as rapidly as it is formed, and if the heat of vaporization is made to come from the vaporizing liquid itself, by thermally insulating it from other sources of heat, then the temperature of the liquid residue may be reduced to the temperature of the triple point of the substance. In this condition the liquid may be both freezing and boiling at the same time. Continued evaporation will convert the substance completely into a solid, and the temperature may be lowered even below that of the triple point. In this way Dewar was able to solidify hydrogen in 1899 and Keesom succeeded in solidifying helium in 1926.

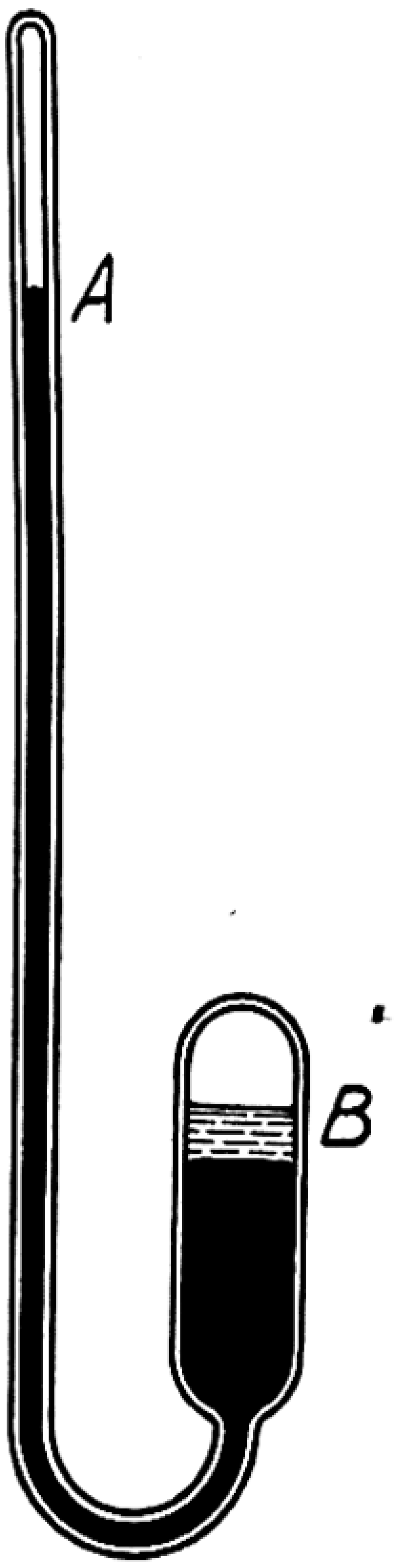

FIG. 94. Apparatus of de La Tour to demonstrate the critical point.

THE CRITICAL POINT

Experiment of de La Tour. The maximum temperature at which a liquid and its saturated vapor can coexist in equilibrium is the critical temperature. The pressure of the saturated vapor at this temperature is the critical pressure. One of the first experiments having to do with the condition of a substance at its critical temperature was carried out in 1822 by Cagniard de La Tour.[18] The apparatus employed in this investigation is illustrated in Fig. 94. Tube *A*, calibrated as to volume, contains air under pressure, and tube *B* contains the substance being investigated. The two are connected by a column of mercury. As the temperature of the whole system is slowly increased, at a certain definite temperature the apparent surface separating the liquid and vapor in tube *B* suddenly disappears. The observed compression of the permanent gas in tube *A* allows the determination of the pressure in tube *B* since both are in contact with the connecting column of mercury. This pressure may be expressed as a function of the temperature. The resulting pressure-temperature curve is found to show a discontinuity at the temperature at which the meniscus disappears.

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[18] C. Cagniard de La Tour, *Ann. chim. phys.*, **21**, 127 (1822).

If this experiment is repeated, with varying amounts of liquid in B at the start of the experiment, as was done by Cailletet and Colardeau,[19] results as shown in Fig. 95 are obtained. For the lower portion of the curve the pressure is independent of the amount of substance present.

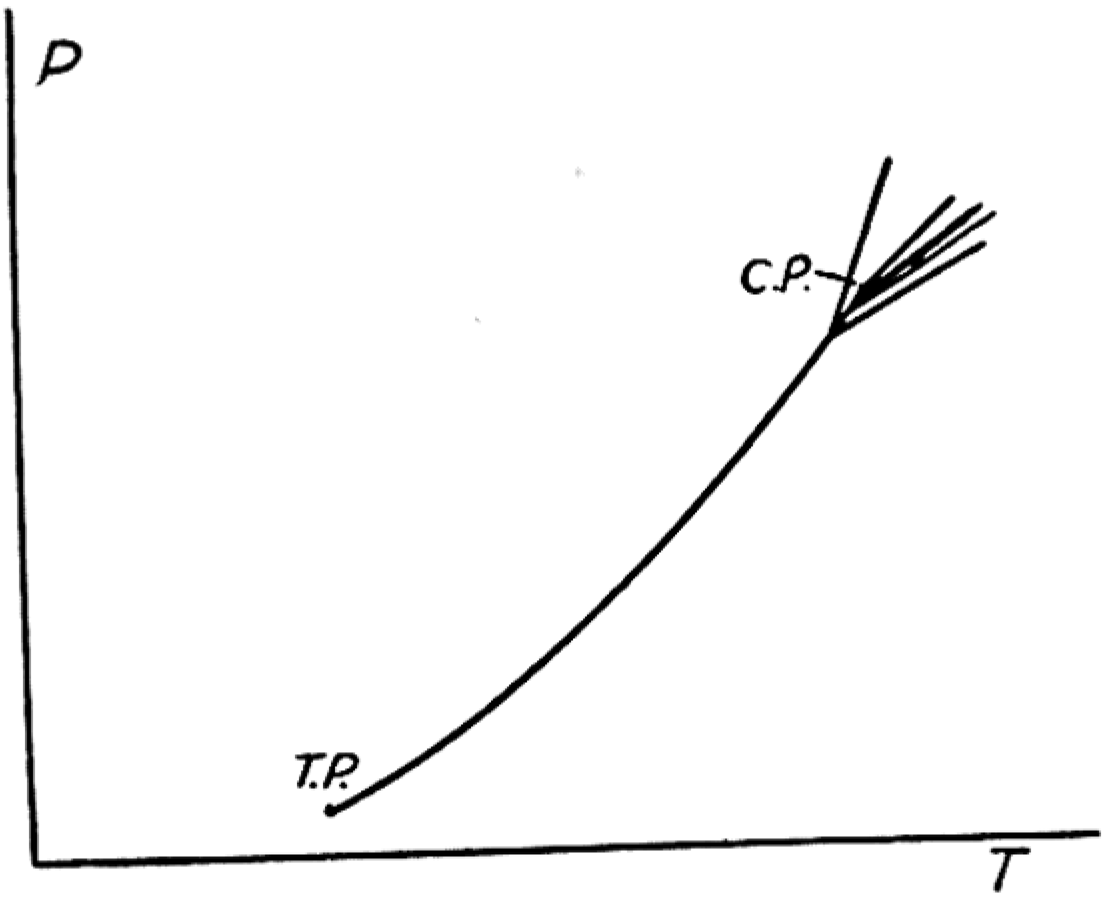

FIG. 95. Vapor-tension curves for varying amounts of substance.

Above the point of discontinuity each curve is linear, the slope being proportional to the amount of substance at the start. Of these curves it will be seen that only for the one at which the discontinuity occurs at the highest temperature are the true values for the critical pressure and the critical temperature the coordinates of the point of discontinuity.

Experiment of Andrews. In 1869, Andrews[20] carried out a very careful investigation of the volume occupied by a definite amount of carbon dioxide at various temperatures as the pressure to which it was subjected was altered. These results are summarized in Fig. 96 as isothermal lines on a pressure-volume coordinate plot. The area enclosed by the dotted line represents the existence of liquid and gaseous phases together. The isotherm passing through the top of this area was found to have the value of the critical temperature 30.95° C. The present generally accepted value for carbon dioxide is 31.1° C. The saturated vapor pressure at the temperature of the critical point is the critical pressure. This pressure was found to be about 73 atmospheres. The volume occupied by 1 gm. of the substance at the critical temperature when exposed to the critical pressure is the critical volume.

At temperatures considerably above the critical temperature the isotherms approach in form the hyperbolas characteristic of Boyle's law.

The variation in the position of the discontinuity in Fig. 95 with a variation in the amount of substance is explainable from Fig. 96. If the amount of substance in the tube *B* is too great, then as the pressure is increased the boundary of the liquid-gas area is crossed at some point on the left of C.P. such as *m*. In this case the meniscus will disappear at the top of the tube as if the tube were completely filled with liquid at the higher pressure. If the amount of material is too small the boundary will be crossed at some point on the right such as *n*. In this case the meniscus will disappear near the bottom as if the tube were filled with gas at the higher pressure. In both cases the temperature at which the meniscus disappears is less than the true critical value, and only by choosing the proper amount of substance will the critical temperature be observed. Owing to the fact that the curve *m* to *n* is rather flat topped, the temperature at which the meniscus disappears does not alter greatly with a slight change in the amount of substance.

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[19] L. Cailletet and E. Colardeau, *Jour. Phys.*, **8**, 389 (1889).

[20] T. Andrews, *Phil. Trans.*, **159**, 575 (1869); **167**, 421 (1876).

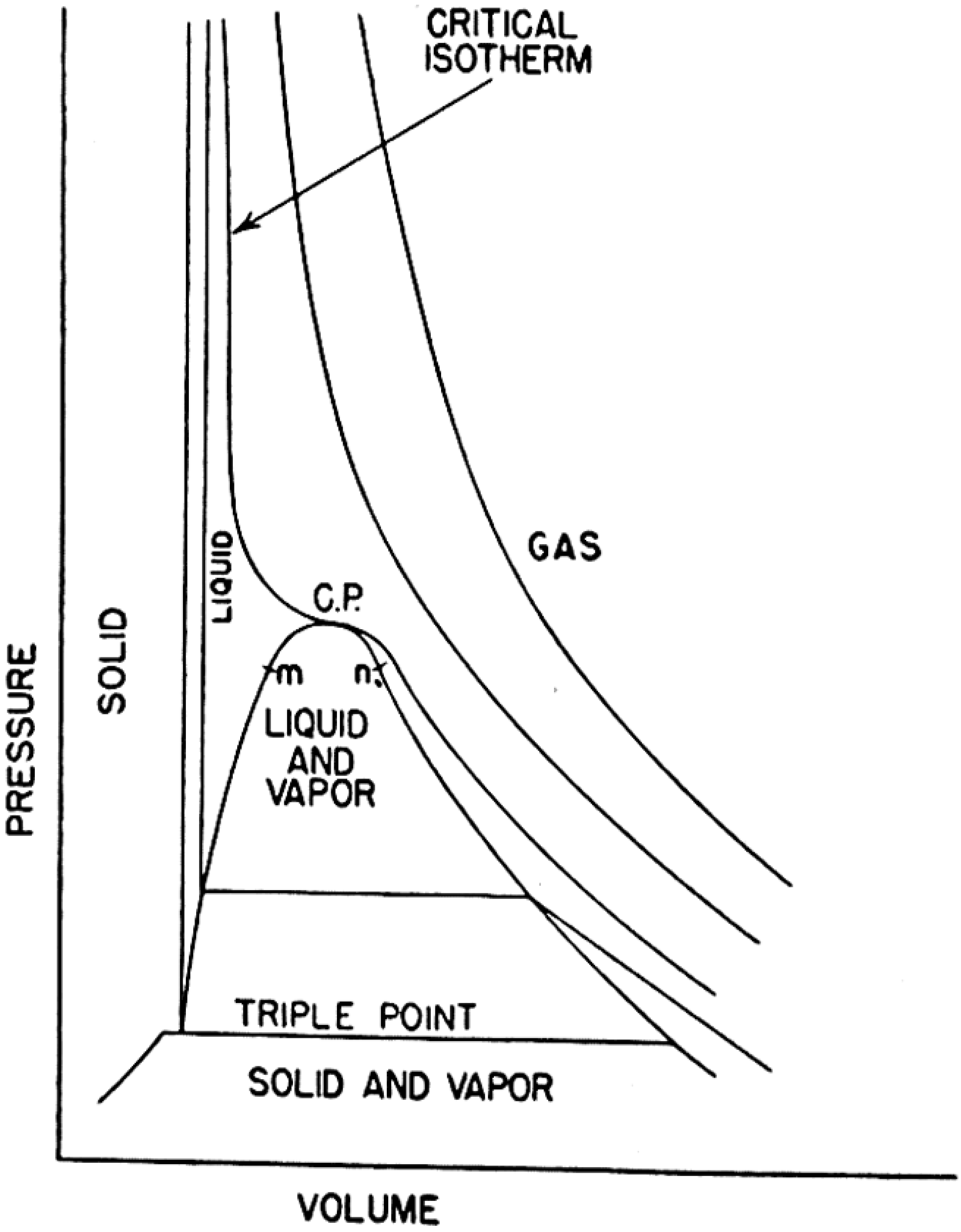

FIG. 96. Pressure versus volume relationship for a substance that expands on melting.

At sufficiently reduced temperatures, namely, −59° C. for carbon dioxide, an isotherm will exist which separates the region (gas-liquid) from another area (gas-solid) below it. Thus the triple point is represented in Fig. 96 by a line.

State of Matter near the Critical Point. The disappearance of the separating surface between the liquid and the gas as observed in tube *B*, Fig. 94, leads to conjecture as to the state of the matter then existing in the tube. Certain arguments indicate that, although the apparent surface has disappeared, the material at the top of the tube is still unlike that at the bottom. Others, perhaps more conclusive, lead to the belief that after the disappearance of the meniscus the entire material in the tube is the same.

For the first-mentioned point of view a rather striking experiment was carried out by Cailletet and Hautefeuille.[21] This consisted in inserting a quantity of iodine with the carbon dioxide in the tube. The absorption spectrum characteristic of the vapor of iodine is different from that of iodine in solution. Absorption tests showed that, before the disappearance of the meniscus, iodine vapor existed above the meniscus and iodine in solution below it. After the elevation of temperature and the disappearance of the separating surface, the absorption tests continued to give the same distinctive results.

On the other hand, experiment shows that at the critical temperature the densities of the liquid and the vapor are the same. Combined with this are the facts that the pressure and the temperature of the two forms are identical, and that there is no free surface of separation. The absence of the separating surface implies equivalent intermolecular attractions. These considerations make any supposition of inequality of state seem unlikely. This point of view was upheld by an additional experiment of Cailletet and Hautefeuille. In this experiment a few drops of a blue oil of galbanum were dissolved in the liquid carbon dioxide, coloring it blue and contributing no color to the vapor. Upon the disappearance of the meniscus the oil settled out as a blue liquid at the bottom of the tube.

Variation in Liquid and Vapor Densities with Temperature. An experiment to observe the variation in the density of a liquid and its saturated vapor, as the temperature changes up to the critical temperature, was carried out by Amagat.[22] In this experiment, the substance under investigation, while maintained at a constant temperature, was compressed so that a portion of the volume of vapor $(\Delta V)_V$ condensed into an increase in the volume of liquid $(\Delta V)_L$. These small changes in volume were observed. The following equation may then be written, where ρ_L and ρ_V denote respectively the density of liquid and density of vapor,

$$\rho_L(\Delta V)_L = \rho_V(\Delta V)_V \tag{20}$$

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[21] L. Cailletet and P. Hautefeuille, *Compt. rend.*, **92**, 840 (1881).

[22] E. H. Amagat, *Compt. rend.*, **114**, 1093 (1892).

If the total mass of substance M is known, then

$$\rho_L V_L + \rho_V V_V = M \tag{21}$$

From these two equations the values of ρ_V and ρ_L may be found for that particular temperature.

A rather simple experimental arrangement leading to these values of the densities of liquid and vapor, as well as the critical density and the critical temperature, has been described by the author.[23] The apparatus employed is shown in Fig. 97. Three thick-walled glass tubes, calibrated as to volume, are filled with varying amounts of the substance under investigation: M_1, M_2, and M_3. (Two tubes only are necessary.) These tubes are now mounted side by side in a uniformly heated furnace at a constant temperature. The volumes of liquid V_L and vapor V_V in each tube are observed by means of a cathetometer. It thus follows that, if ρ_L and ρ_V denote respectively the density of the liquid and the density of the vapor, then,

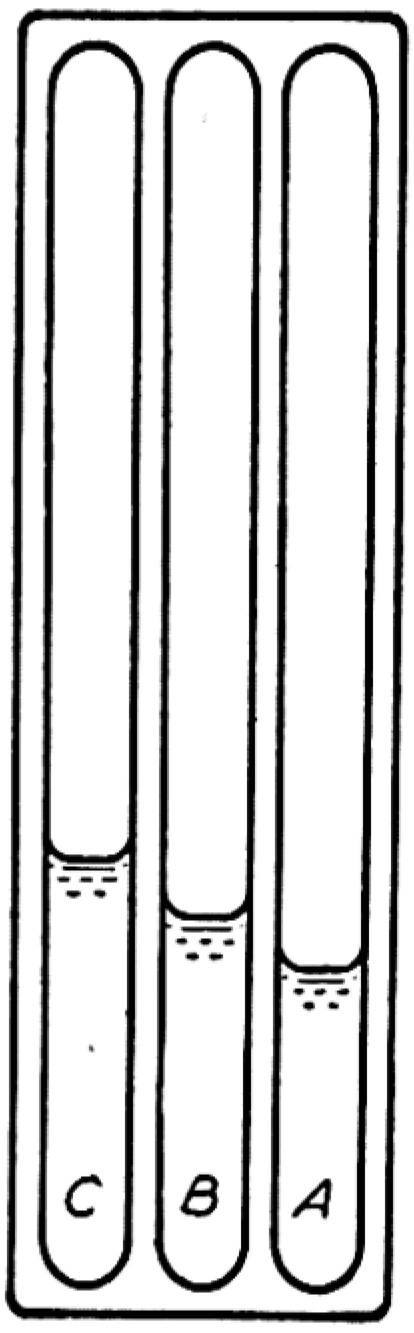

FIG. 97. Tubes filled with varying amounts of a substance to determine the critical constants.

$$\rho_L V_L + \rho_V V_V = M_1 \tag{22}$$

and

$$\rho_L V_L' + \rho_V V_V' = M_2, \text{ etc.} \tag{23}$$

The graphical solution of these equations yields readily the values of ρ_L and ρ_V at the temperature employed.

The values of the densities obtained at successive temperatures as the critical value is approached are shown collectively in Fig. 98. This demonstrates that there is a decrease in ρ_L and an increase in ρ_V as the temperature increases, so that the two densities meet at the common value of the critical density at the critical temperature. The averaged values of ρ_L and ρ_V are found to lie very closely along a straight line. By making a preliminary test, the amount of material in one of the tubes may be adjusted so that the meniscus in it will disappear at the critical temperature.

EQUATIONS OF STATE

Van der Waals' Equation. The results of Andrews, Fig. 96, show clearly that at low temperatures the isothermal lines are not represented by the expression for Boyle's law $P = c/V$. The first equation of state meeting with success in representing the observed data was developed by J. van der Waals[24] in 1877. The physical interpretation of the modifications in the gas law, $PV = RT$, that were proposed may be very simply pictured. Thus in Fig. 99 the gas in an element of volume (ΔV) adjacent to a surface upon which the pressure is to be measured does not exert upon this surface the full pressure of which it should be capable. According to the Newtonian universal law of gravitation any volume of gas near the surface is experiencing a force away from the surface due to the rest of the gas, that is proportional to the product of the attracting and attracted masses. This results in a cohesive pressure that is proportional to the square of the density or inversely proportional to the square of the specific volume of the gas. Thus the total pressure which should be employed in the gas law is the observed value P plus a correction term a/V^2. The term a/V^2 is referred to as the cohesive pressure, and $(P + a/V^2)$ is called the thermal pressure; a is a constant, characteristic of the gas.

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[23] J. M. Cork, *Rev. Sci. Inst.*, **1**, 563 (1930).

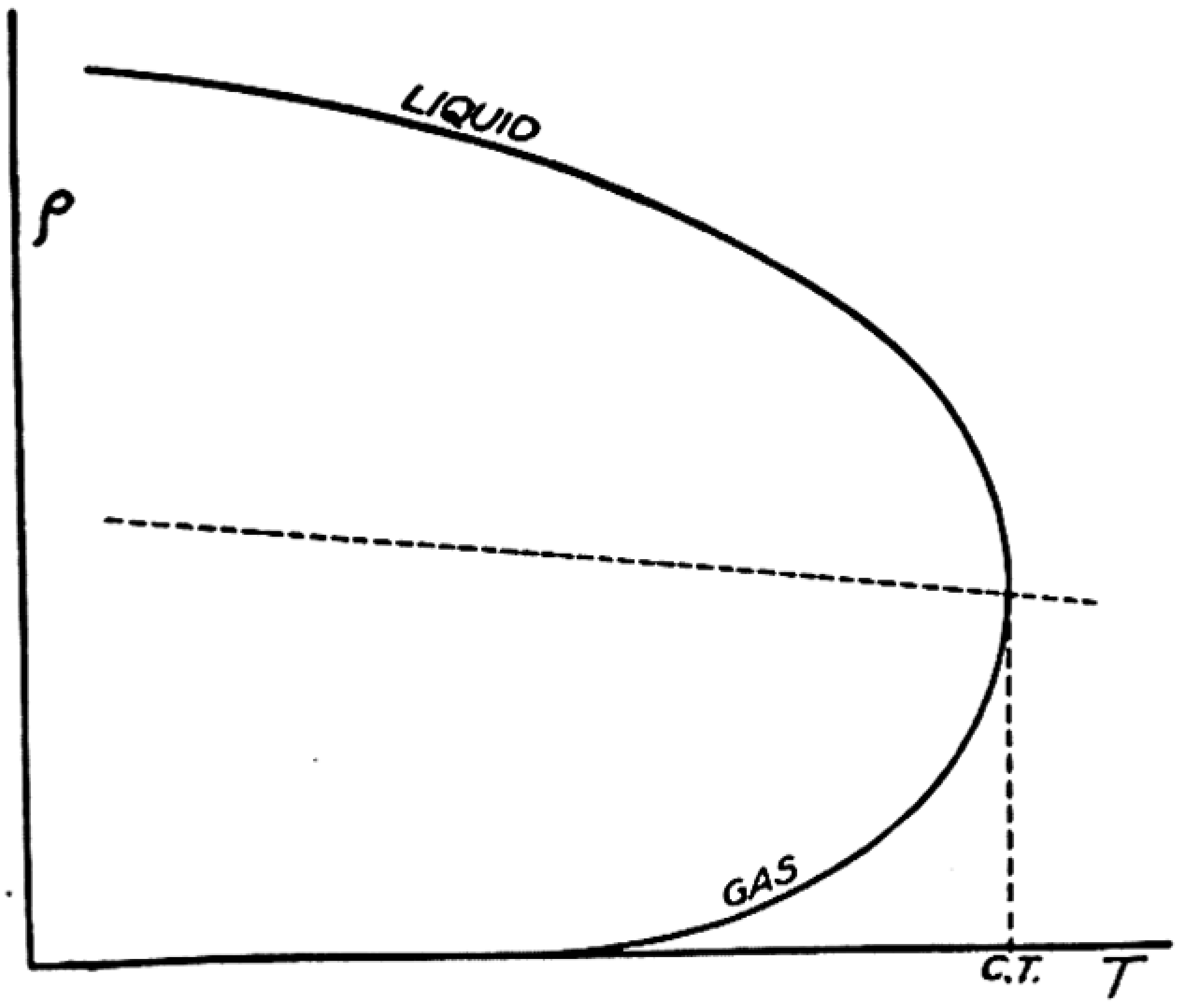

FIG. 98. The variation in the density of a liquid and its saturated vapor with temperature.

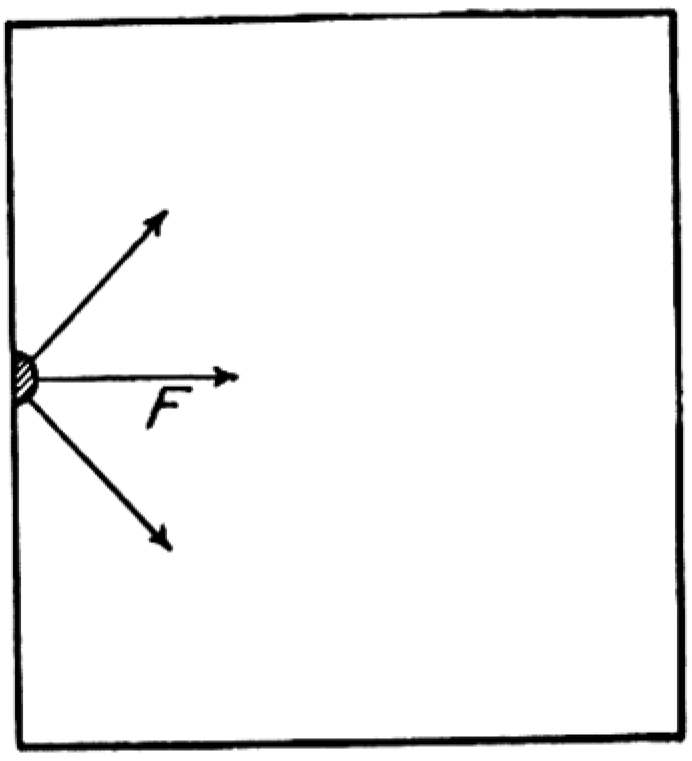

FIG. 99. To illustrate cohesive pressure within a gas.

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[24] J. van der Waals, *Annal. phys. chem. Beibl.*, 1, 10 (1877).

Moreover, when the volume of the gas is altered, it is the space between the particles which changes. Hence the volume that is effective in the gas law should be the apparent volume V, minus a constant term b which might be expected to represent the minimum possible volume of packing for the gas particles. If they are assumed to be spheres that are arranged in a close packing array such as a face-centered cubic structure, then the minimum volume is 1.37 times the actual volume occupied by the particles. Actually, however, from kinetic theory, assuming spherical particles, the constant b is shown to be four times the actual volume of the gas molecules so that

$$b = \tfrac{16}{3} N' \pi r^3 \tag{24}$$

where N' means the number of molecules per gram-mole and r is the radius of the molecule. The complete expression for the gas law is then

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{25}$$

or in powers of V

$$V^3 - \frac{Pb + RT}{P} \cdot V^2 + \frac{a}{P} \cdot V - \frac{ab}{P} = 0 \tag{26}$$

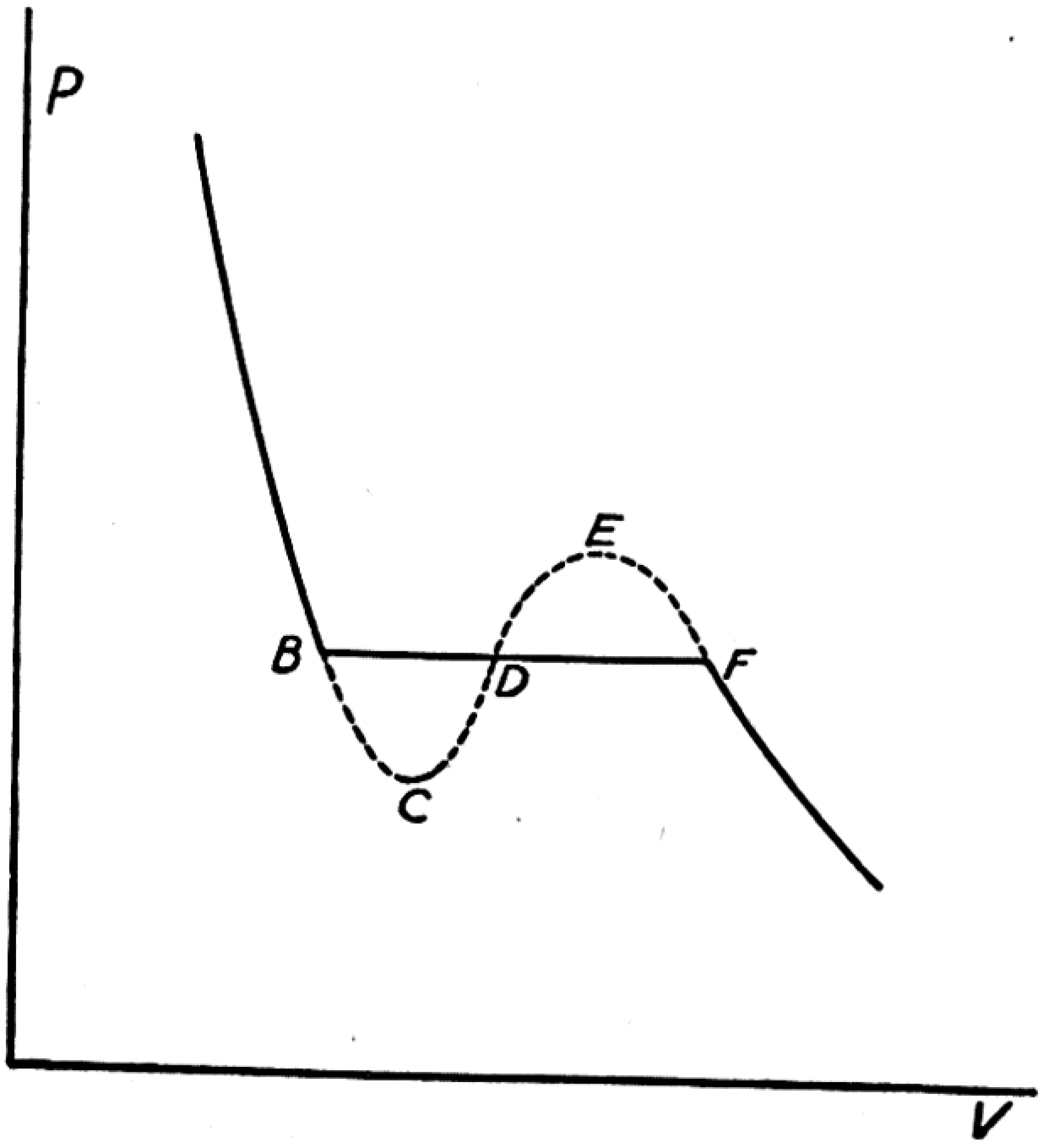

FIG. 100. Isotherm representing the equation of van der Waals.

This cubic equation in V is shown graphically for a particular value of T in Fig. 100. As early as 1871, Thomson[25] had suggested an isotherm of this ideal form to represent the actual performance of a substance. Normally the curved portion between B and F is not observed in evaporating a liquid or condensing a vapor into a liquid. By careful manipulation a portion BC, corresponding to a superheated liquid, or a portion EF representing a supersaturated vapor may be demonstrated.

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[25] J. Thomson, *Brit. Assoc. Report*, **41**, 31 (1871).

The three roots of equation 26 may be real as given by the intersections of an isobar with the curve at B, D, and F. Another possibility is that only one of the three roots is real and that the remaining two are imaginary. This will be the case at very high and at low pressures.

The form of equation suggested by van der Waals finds justification also in kinetic theory. If the molecules are regarded as elastic spheres, then the momentum communicated to the walls is influenced by two factors. One of these is the actual volume of the gas particles which results in a reduced mean free path or more impacts per second and hence a greater pressure. The other consideration is the time required for the separation of two molecules after collision. If this is large the momentum communicated to the walls is reduced and hence also the apparent pressure.

The Constants in the Equation of Van der Waals and the Critical Constants. At the critical point, the three real roots of equation 26 are equal. At this point $V = V_c$, and hence,

$$(V - V_c)^3 = V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0 \tag{27}$$

Equation 27 must be an identity with equation 26 if T and P are there given the critical values T_c and P_c. By equating the coefficients term by term it follows that

$$\frac{P_cb + RT_c}{P_c} = 3V_c, \quad \frac{a}{P_c} = 3V_c^2 \quad \text{and} \quad \frac{ab}{P_c} = V_c^3 \tag{28}$$

From which

$$\left.\begin{aligned} P_c &= \frac{a}{27b^2} \\ T_c &= \frac{8a}{27Rb} \\ V_c &= 3b \end{aligned}\right\} \tag{29}$$

or

$$\left.\begin{aligned} a &= 3P_cV_c^2 \\ b &= V_c/3 \\ R &= \frac{8}{3}\frac{P_cV_c}{T_c} \end{aligned}\right\} \tag{30}$$

and

A similar result may be obtained by expressing equation 25 as

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{31}$$

and forming dP/dV and d^2P/dV^2 at the critical point, where $T = T_c$ and $V = V_c$. Since the critical point is a point of inflection on the critical isotherm, both derivatives may be set equal to zero. Their solution yields the results shown in equations 29.

From equations 29, one may form the fraction RT_c/P_cV_c. This expression for an ideal gas would be unity. Hence it shows the deviation at the critical point and is as follows:

$$\frac{RT_c}{P_cV_c} = \frac{R \times \dfrac{8a}{27Rb}}{\dfrac{a}{27b^2} \times 3b} = \tfrac{8}{3} = 2.67 = K \tag{32}$$

For actual gases it is found that the value for this expression is greater than 2.67. Thus for oxygen K is equal to 3.42 and for carbon dioxide the magnitude is 3.61. Such a discrepancy is not unexpected as the van der Waals equation is admittedly not satisfactory for the condensed state.

Hence from the experimental values of P, V, and T, for any three conditions of the gas, three simultaneous equations may be obtained whose solution gives the van der Waals constants. From these values the critical constants P_c, V_c, and T_c may be deduced by equation 29. Critical constants for a few common substances are shown collectively in Table 13.

Reduced Equation of State. The pressure, volume, and temperature of a gas may be expressed in terms of the values for each at the critical point. Thus

$$P = xP_c,\ V = yV_c \quad \text{and} \quad T = zT_c \tag{33}$$

x, y, and z, are thus numbers whose values are unity when P, V, and T have the values characteristics of the critical point.

If these quantities as well as the values of a and b from equation 30 are substituted in equation 26, it follows that

$$y^3 - \left(\frac{1}{3} + \frac{8z}{3x}\right)y^2 + \left(\frac{3}{x}\right)\cdot y - \frac{1}{x} = 0 \tag{34}$$

Thus the constants characteristic of the particular substance have entirely disappeared and an identical expression is obtained for all gases. Equation 34 is a cubic in y in the same way that equation 26 was a

TABLE 13

CRITICAL CONSTANTS OF SOME COMMON SUBSTANCES

Substance		Critical		
Name	Symbol	Temperature	Pressure	Density
Helium	He	−267.9° C.	2.26 atm.	0.0693 $\frac{\text{gm.}}{\text{cm.}^3}$
Hydrogen	H_2	−239.9	12.8	0.031
Nitrogen	N_2	−147.1	33.5	0.311
Air	$N_2 + O_2$	−140.7	37.2	0.35
Carbon monoxide	CO	−139	35	0.311
Oxygen	O_2	−118.8	49.7	0.430
Methane	CH_4	− 82.5	45.8	0.162
Krypton	Kr	− 63	54	0.78
Ethylene	C_2H_4	9.7	50.9	0.22
Carbon dioxide	CO_2	31.1	73	0.460
Ethane	C_2H_6	32.1	48.8	0.21
Acetylene	C_2H_2	36.0	62	0.231
Nitrous oxide	N_2O	36.5	71.7	0.45
Ammonia	NH_3	132.4	111.5	0.235
Chlorine	Cl_2	144	76.1	0.573
Sulphur dioxide	SO_2	157.2	77.7	0.52
Pentane	C_5H_{12}	197.2	33	0.232
Ethyl alcohol	C_2H_6O	243.1	63.1	0.275
Carbon tetrachloride	CCl_4	283.1	45	0.558
Benzene	C_6H_6	288.5	47.7	0.304
Toluene	C_7H_8	320.6	41.6	0.292
Water	H_2O	374	217.7	0.40

cubic in V. The pressure-volume and pressure-temperature relationships for a substance when expressed in terms of x and y and x and z may be illustrated as shown in Fig. 101. These diagrams are exactly the same for all gases. Hence if one has complete information regarding any one substance, and data regarding any other substance at one point, then complete information regarding the second substance may be deduced.

Illustration. Having complete data regarding the variation of vapor tension with temperature for water and knowing the data for oxygen at the critical point, find the normal boiling point of oxygen. The critical temperature and the critical pressure for water are respectively 374° C. and 217.7 atmospheres, and for oxygen the corresponding values are −118° C. and 50 atmospheres. At its normal boiling point the value of y for oxygen is thus 1/50 and therefore water under a corresponding condition must be subjected to a pressure of 4.354 atmospheres. From the complete vapor tension data for water (see Table 19, Appendix) it is found that at 4.354 atmospheres its temperature is 147° C. or 420/638 of its critical temperature. Thus this value for z of 420/638 or (0.648) is associated always with a y value of 0.02. Now 0.648 of the critical temperature of oxygen, i.e., 155° K., is 100° K. or −173° C. This then is the expected boiling point and is to be compared with the experimental value of −182.7° C. Considering the wide difference in nature between the two substances and the fact that the reasoning is based upon the equation of van der Waals, which under certain conditions is known to be far from satisfactory, the agreement is not bad.

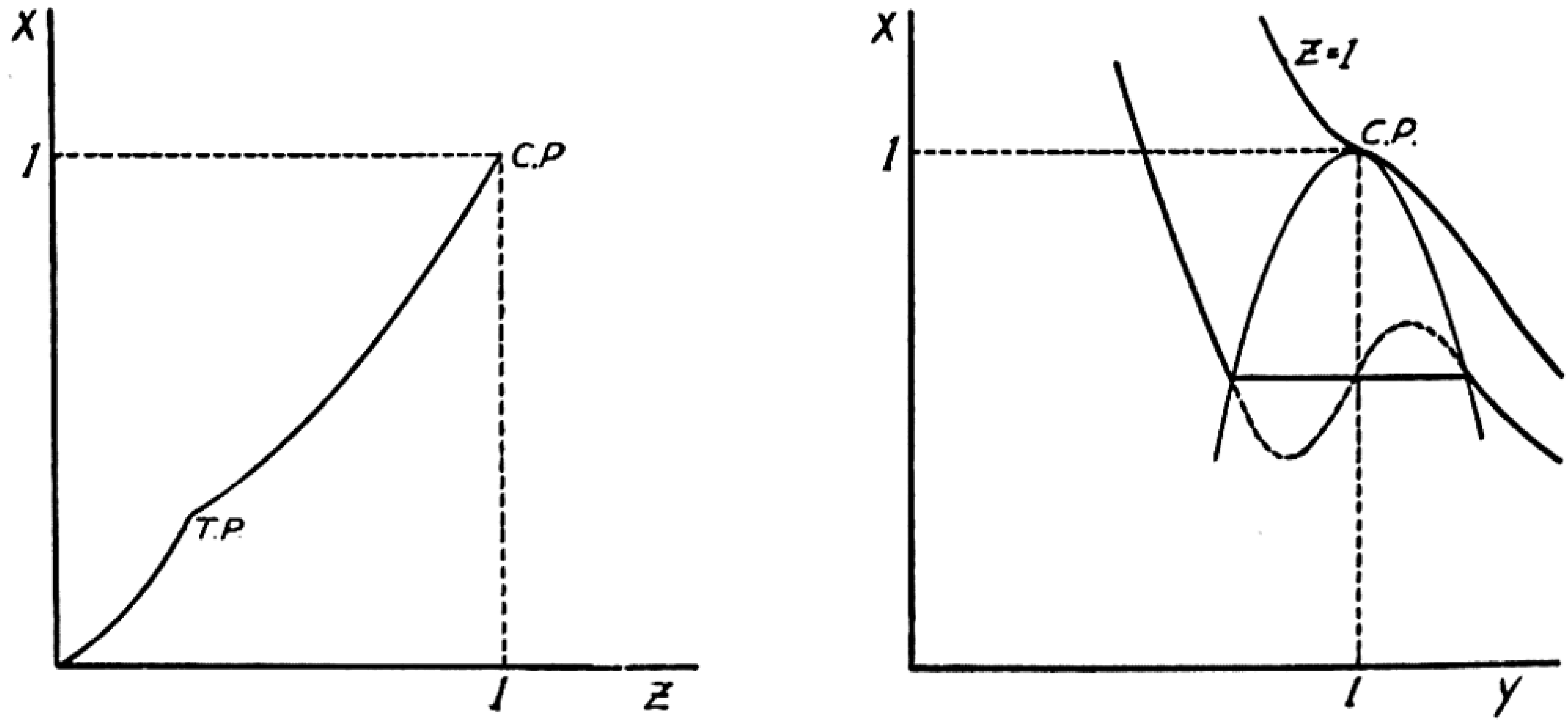

FIG. 101. Diagrams representing the reduced equation of state.

TABLE 14

TRIPLE-POINT DATA FOR SOME COMMON SUBSTANCES

Substance		Temperature	Pressure
Name	Symbol		
Helium	He	<−273° C.	......
Hydrogen	H_2	−259.1	51.4 mm. Hg
Neon	Ne	−248.6	325
Oxygen	O_2	−218.4	2
Nitrogen	N_2	−209.8	96.4
Argon	A	−189.2	512.2
Krypton	Kr	−169	132.5
Xenon	X	−140	......
Chlorine	Cl_2	−103	8.9
Ammonia	NH_3	− 77.7	44.2
Sulphur dioxide	SO_2	− 72.7	16.3
Carbon dioxide	CO_2	− 56.6	3880
Mercury	Hg	− 39	0.00000124
Water	H_2O	+ 0.0075	4.579

It might be expected that the reduced triple-point data would be identical for every substance. This is true only for substances that are closely related.

Table 14 shows collectively the available data on the triple point for a few substances. The values of the temperatures at the triple point are practically the normal freezing points of the substances, since the change of freezing point with pressure is very small.

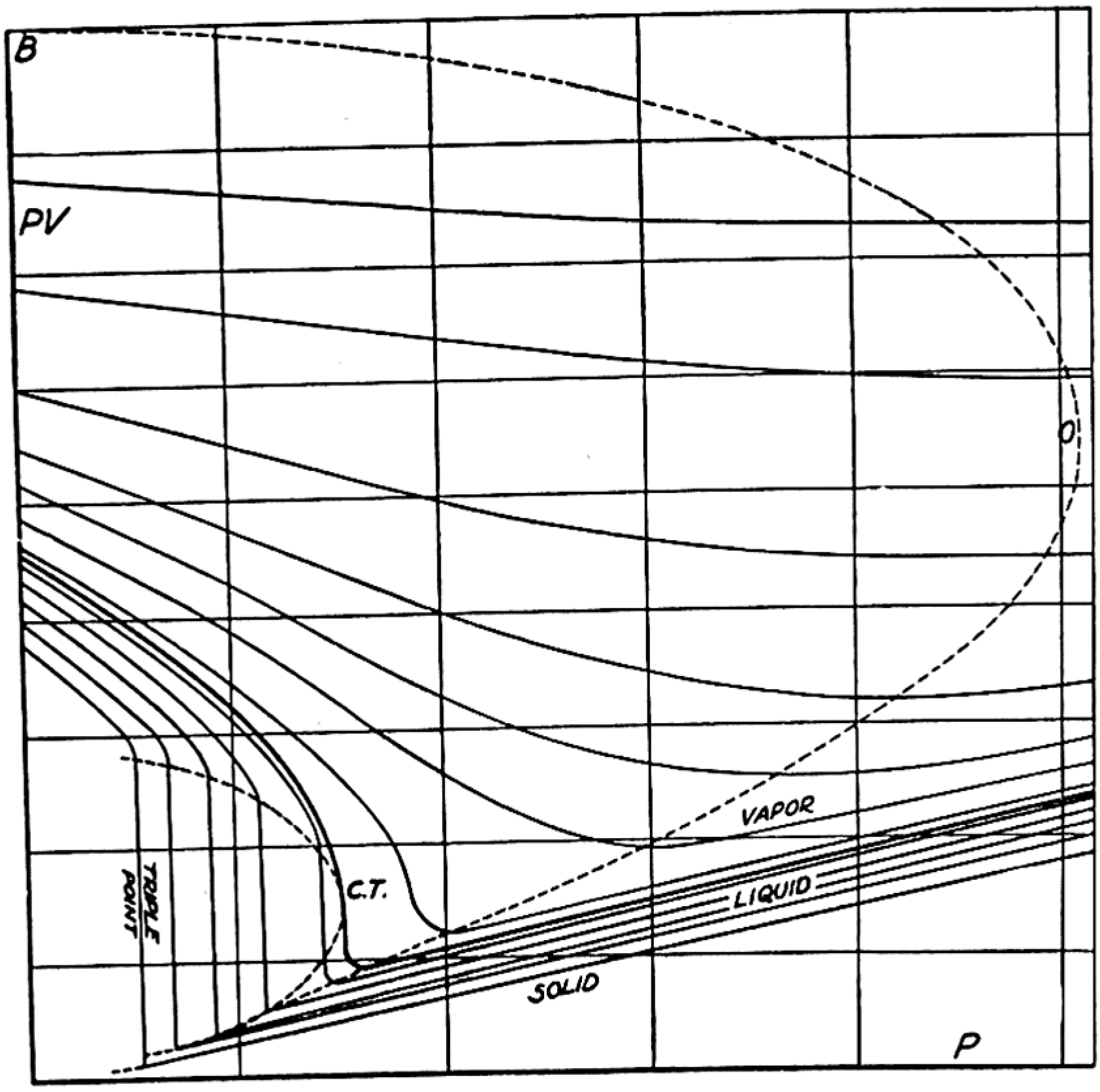

FIG. 102. Isothermals of carbon dioxide on a *PV* versus *P* coordinate plot.

Pressure — *PV* Diagram. The manner in which a gas deviates from the ideal gas law may be strikingly portrayed by representing its condition on a *PV* versus *P* coordinate plot. Figure 102 illustrates in this way the data for carbon dioxide. For pressures not too large and temperatures not too high the slope of each such isothermal is negative for most gases. At very high pressures the curves are almost parallel lines with positive slopes. Hydrogen at ordinary temperatures exhibits isothermals of positive slope but when sufficiently cooled it behaves like other gases. It will be shown later that the slope of this isotherm is a valuable criterion regarding the behavior of the gas when it is allowed to expand through a nozzle. Substances characterized by isotherms with a negative slope are cooled by such an expansion.

For those substances whose isotherms have a positive slope the overall result may be either a cooling or a heating, depending upon the relative magnitude of two effects. See page 246.

In so far as the gas may be represented by the van der Waals relationship a cubic equation in PV follows:

$$(PV)^3 - (bP + RT)(PV)^2 + aP(PV) - abP^2 = 0 \qquad (35)$$

The differentiation of this equation with respect to P, with $d(PV)/dP$ equated to zero, yields a relationship for the minimum value of the isotherm. Hence

$$(PV)^2 - \frac{a}{b}(PV) + 2aP = 0 \qquad (36)$$

These minimum points for successive isotherms thus lie on a parabola shown dotted in Fig. 102. Again differentiating equation 36 with respect to PV and setting $\dfrac{dP}{d(PV)} = 0$, then

$$PV = \frac{a}{2b} \qquad (37)$$

Equation 37 is a relationship existing at the point 0. At the position B, $P \rightarrow 0$. Hence at this point from equation 36, $PV = a/b$. Above point B all gases exhibit positive slopes at all pressures.

Other Equations of State. Although van der Waals' equation appeared to represent well the data of Andrews for carbon dioxide, more exact experimentation yielded results incapable of being fully expressed by such a simple relationship. On this account many later equations[26] have been proposed. Among these may be mentioned the following:

(*a*) *Clausius.* It was pointed out by Clausius[27] that the constant a in van der Waals' equation must itself be a function of the temperature. In addition a third constant (c) was introduced such that an equation of the following form was proposed:

$$\left(P + \frac{a}{T(V + c)^2}\right)(V - b) = RT \qquad (38)$$

Since the equation has four constants instead of three, it naturally is better able to represent the experimental facts.

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[26] For a summary of such equations see Partington and Shilling, *Specific Heat of Gases*, p. 29, 1924.

[27] R. Clausius, *Ann. Physik*, **9**, 337 (1880).

(*b*) *Dieterici.* An equation having the form

$$Pe^{a/RTV}\ (V - b) = RT \tag{39}$$

was suggested by Dieterici.[28] Although involving only the same number of constants as the equation of van der Waals, it is found to be more satisfactory at low pressures.

(*c*) *Berthelot.* Starting with an equation similar to that of Clausius and taking c equal to zero, Berthelot[29] substitutes the values obtained for a and b in terms of the critical constants. From this the following useful equation is obtained:

$$PV = RT\left[1 + \frac{9}{128}\cdot\frac{T_c}{P_c}\cdot\frac{P}{T}\left(1 - \frac{6T_c^2}{T^2}\right)\right] \tag{40}$$

(*d*) *Callendar.* An equation formulated by Callendar,[30] and applying particularly well to steam at not too high pressures, is

$$(V - b) = \frac{RT}{P} - \frac{a}{T^n} \tag{41}$$

In this equation, b was taken as the volume occupied by a gram of the substance in the condensed form (i.e., water) and a and n are constants. n is taken to be equal to half the number of degrees of freedom characteristic of the gas under the condition of constant volume as the pressure is made to approach zero. For steam the value of 10/3 was satisfactory.

(*e*) *Holborn and Otto.* Holborn and Otto[31] have found that isotherms similar to those shown in Fig. 102 characteristic of any gas may be satisfactorily represented by the following empirical equation:

$$PV = A + BP + CP^2 + DP^4 + EP^6 \tag{42}$$

A, B, C, D, and E are constants characteristic of a substance at only one particular temperature. As the temperature of the gas is increased, the importance of E, D, C, etc., vanishes in order. Thus hydrogen at 100° C. is satisfactorily represented by a linear equation. In Table 15 are shown the values found for the necessary constants to represent the behavior of hydrogen and nitrogen at the temperatures −100° C., 0° C., and 100° C.

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[28] C. Dieterici, *Ann. Physik*, **66**, 826 (1898).

[29] D. Berthelot, *Arch. Néerland*, **5**, 317 (1900).

[30] H. L. Callendar, *Proc. Roy. Soc.*, **67**, 266 (1901).

[31] L. Holborn and J. Otto, *Zeit. Phys.*, **33**, 1 (1925).

TABLE 15

EMPIRICAL CONSTANTS TO SATISFY

$PV = A + BP + CP^2 + DP^4 + EP^6$

FOR HYDROGEN AND NITROGEN

Substance	Temperature, °C.	A	$B \times 10^3$	$C \times 10^6$	$D \times 10^9$
Hydrogen	+100	+1.36506	+0.91400	....	....
	0	+0.99918	+0.82094	+0.3745	....
	−100	+0.63344	+0.53700	+1.551	....
Nitrogen	+100	+1.36682	+0.36057	+3.1510	....
	0	+1.00060	−0.60716	+5.4056	....
	−100	+0.63434	−3.04600	−3.0667	+1.8603

(*f*) *Kammerlingh Onnes.* It is equally possible to represent the isotherms of Fig. 102 by equations of other forms. Thus Onnes[32] suggested

$$PV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \frac{E}{V^6} + \frac{F}{V^8} \tag{43}$$

where the constants A, B, C, etc., are functions of the temperature and are called the virial coefficients.

Substances under Very High Pressures. Experiments in which various substances have been subjected to extremely high pressures have been carried out by Bridgman.[33] Under this condition the physical properties of many materials change in a remarkable manner. Thus ice at low temperatures has been shown to exist in at least five allotropic forms. An equilibrium diagram for these forms on a pressure-temperature diagram is shown in Fig. 103. It may be seen from this figure that at high pressures water acts like most other substances; that is, it may be solidified by compression alone. Starting with ordinary ice (form I) at −10° C., an increase in pressure at constant temperature to 1,200 kg. per cm.^{2} will cause it to melt. Now a further increase in pressure to 4,600 kg. per cm.^{2} will again cause it to solidify, this time giving ice (form V). A further increase in pressure to 6,300 kg. per cm.^{2} gives the final high-pressure modification (form VI).

These transformations, as well as similar experiments on other substances such as mercury, suggest the possibility of a more complete equation of state. A satisfactory equation should allow transformations that are continuous between the liquid and solid phases as well as between the vapor and liquid. On a P–V diagram this might result in

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[32] H. Kammerlingh Onnes, and H. R. Kuypers, *Commun. Univ. Leiden*, **169b**, (1924).

[33] P. W. Bridgman, *Proc. Am. Acad.*, **47**, 441 (1912).

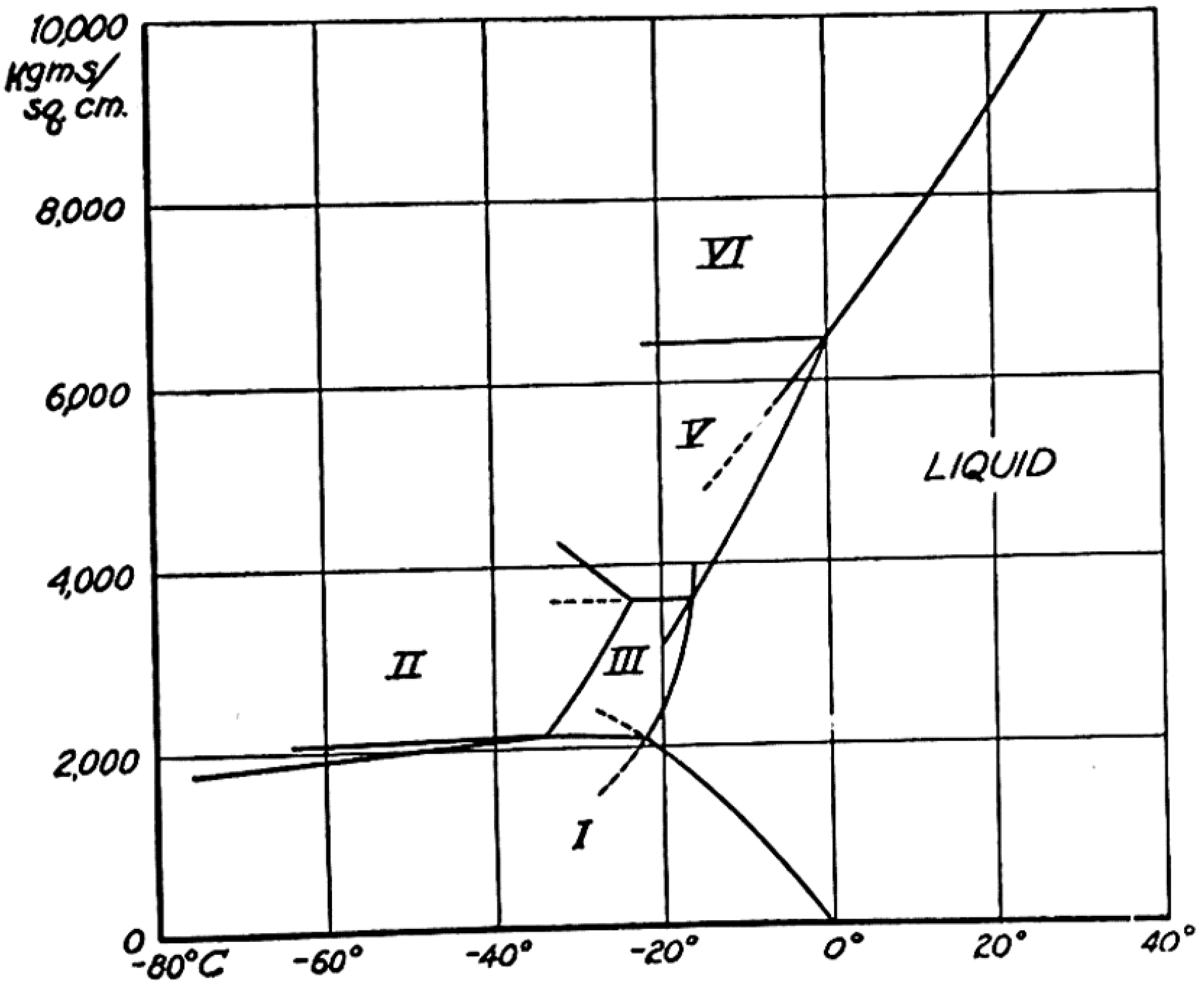

FIG. 103. Modifications of ice with pressure (Bridgman).

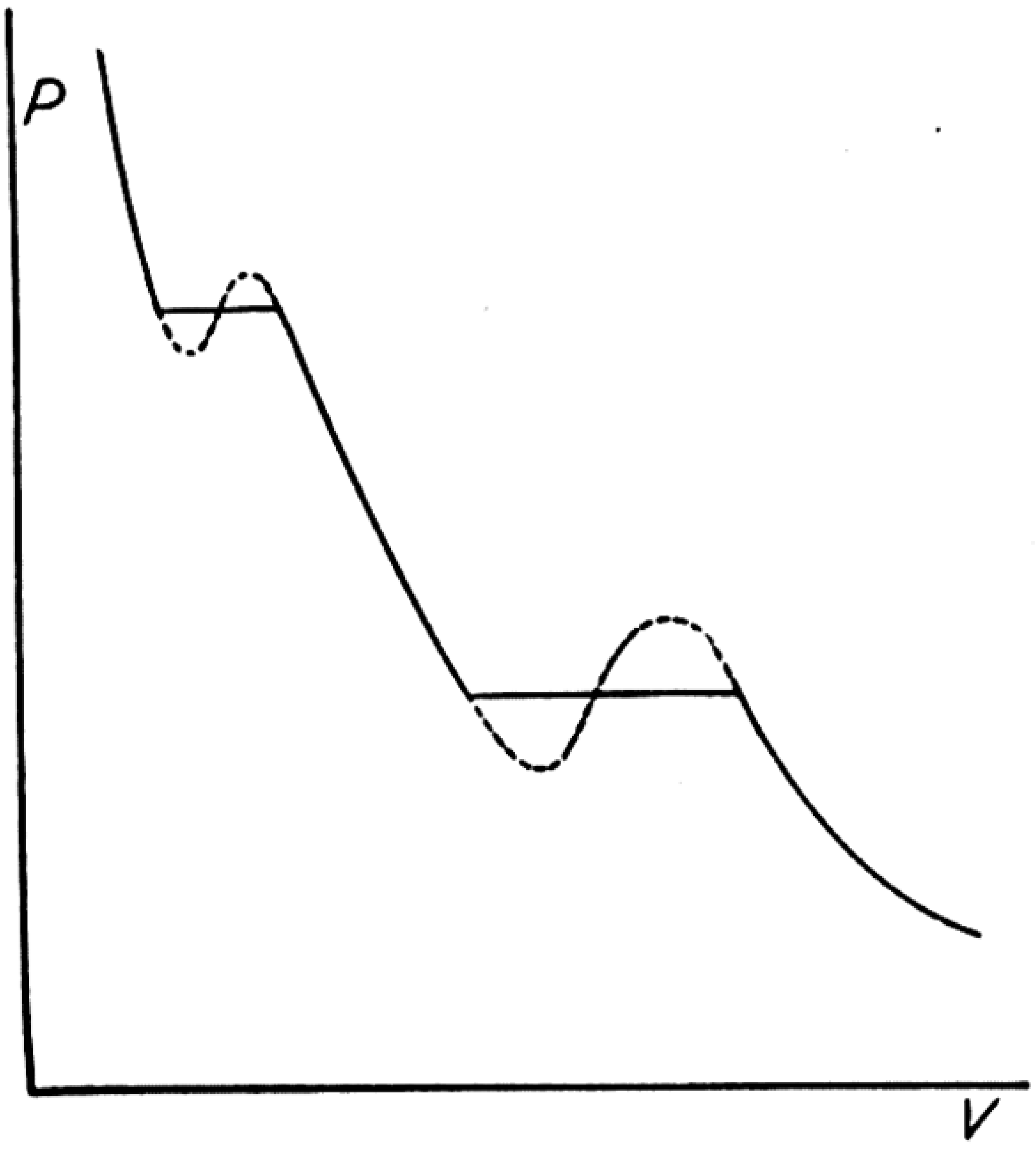

FIG. 104. Isotherm for a sixth degree equation of state embodying the solid phase.

a relationship as shown in Fig. 104 and be represented perhaps by a sixth degree equation in V.

The State of Degeneracy in a Gas and Free Electrons in Metals. By the application of the statistical methods of Maxwell and Boltzmann to the radiation within an enclosure, it was possible to deduce a law for the spectral distribution in the radiant energy from a black body. The radiation was considered as composed of light quanta, called photons. Until 1924 such calculations always resulted in the Wien law rather than the more exact Planck relationship. At this time an important modification in the theory of statistics was introduced by Bose.[34] In this, the necessity of distinguishing between the individual quanta was disregarded. This new method gave directly the desired Planck law.

The success of this assumption in the field of radiation led Einstein[35] to apply the same principle to monatomic gases. The results in this case were in many particulars not satisfactory. In the application to gases it becomes necessary to quantize the linear motion of the particles. Thus a gas particle may in a sense be regarded as having a frequency ν determined by the dimensions of the container, the velocity v of the particle, and the number of other particles present, so that if l is an effective free path then ν may be taken as $v/2l$. Then by applying the result of the Planck theory, that the energy of the oscillator is an integral multiple of $h\nu/2$, it follows that the kinetic energy E is

$$E = \tfrac{1}{2}mv^2 = n \cdot \frac{h}{2} \cdot \frac{v}{2l} \tag{44}$$

From this

$$v = \frac{nh}{2ml} \quad \text{and} \quad E = \frac{n^2h^2}{8ml^2} \tag{45}$$

Thus the velocity of the particle and its energy assume only quantumly determined values.

On the basis of Pauli's " exclusion principle " (i.e., that no two molecules in a gas can have the same set of quantum numbers), a still further modification in the theory of statistics was proposed by Fermi[36] in 1926. Dirac[37] independently arrived at a similar result from the wave-mechanic point of view. As a result of this modification, many problems dealing with atoms and molecules could be solved for the first time.

Sommerfeld[38] applied the same statistics to the free conduction electrons in metals. He showed that if the following expression represented by A is very small compared to unity:

$$A = \frac{V(2\pi mkT)^{3/2}}{h^3} \lll 1 \tag{46}$$

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[34] S. N. Bose, *Zeit. Phys.*, **27**, 384 (1924).

[35] A. Einstein, *Sitz. preuss. Akad. Wiss.*, **22**, 261 (1924).

[36] E. Fermi, *Zeit. Phys.*, **36**, 902 (1926).

[37] P. A. M. Dirac, *Proc. Roy. Soc.*, **112**, 661 (1926).

[38] A. Sommerfeld, *Zeit. Phys.*, **47**, 1 (1928).

where V is the volume per particle, m is the mass of the particle, k is the Boltzmann gas constant, T is the absolute temperature, and h is the Planck constant, then the Maxwellian distribution law may no longer be expected to hold. In this condition the gas is called a degenerate gas. At a sufficiently low temperature all substances must approach this state. For the free electron gas in metals (assuming a number of electrons equal to the number of mass particles) at ordinary temperatures A has a value of only one ten-thousandth, approximately, and hence the gas is degenerate. This small value is due to the extremely small mass of the electron.

Some of the results that follow are:

(*a*) The mean velocity of electrons is to a first approximation independent of the temperature.

(*b*) Their expected contribution to the atomic heat is negligible, as experimentally demanded.

(*c*) A more satisfactory value (3.3) is obtained for the constant in the Wiedemann-Franz law relating thermal and electrical conductivities.

(*d*) A zero point energy exists for gases. For free conduction electrons, as assumed, this average value was estimated as being about 3 electron-volts.

(*e*) The existence of a zero point pressure is essential. Thus a modification in the fundamental gas laws at very low temperatures is necessary. Such a modification had been proposed by Sackur[39] as a result of his determination of the chemical constant of hydrogen at low temperatures.

Helium at Low Temperatures. At very low temperatures helium exhibits certain most unusual properties. Unlike all other substances no indication of a triple point exists. If the density of liquid helium is observed as it is cooled toward absolute zero, it is found[40] that it increases progressively until a temperature 2.16° K. is attained at which the density is 0.146 gm. per cm.^{3} Upon further cooling the density begins to decrease. If the pressure is increased during the cooling, the temperature at which the change in density reverses is lower, so that it occurs at 1.8° K. for a pressure of 30 atmospheres. The locus of these temperatures of transition is called the λ line and is shown in Fig. 105, line A to B. At higher temperatures, shown to the right of the line, the liquid is designated as helium I and it behaves much as other liquids. At temperatures below the λ line the liquid is termed helium II and it behaves in an extraordinary manner. While most physical properties change abruptly as the λ line is crossed, no evidence could be found[41] for the existence of a latent heat which should be present to characterize a true transition point.

The thermal conductivity of helium II is enormously large. At

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[39] O. Sackur, *Ber. deut. chem. Ges.*, **47**, 1318 (1914).

[40] H. Kammerlingh Onnes and J. D. A. Boke, *Commun. Univ. Leiden*, **170b**, 1924.

[41] W. H. Keesom and A. P. Keesom, *Physica*, **3**, 359 (1936).

1.8° K. it was found[42] to be 810 cal. cm.$^{-1}$ sec.$^{-1}$ deg. C.$^{-1}$ which is more than 800 times the value for copper at ordinary temperatures. The liquid will creep along a surface at a rapid rate so that a flask partly lowered into the liquid will gain or lose helium II as if the flask were porous. The viscosity of helium II at 1.2° K. is[43] about 1.5 micropoise which is a value less than one-fiftieth the viscosity of hydrogen gas at ordinary temperatures. On being warmed the specific heat of helium II increases from 0.2 cal. per gm. per deg. C. at 1.3° K. up to about 6 cal. per gm. per deg. C. at 2.18° K. On increasing the temperature giving helium I there is an abrupt drop to about 0.6 cal. per gm. per deg. C. The freezing point curve has been extended up to pressures greater than 5,000 atmospheres, under which condition solid helium may exist at temperatures as high as 40° K.

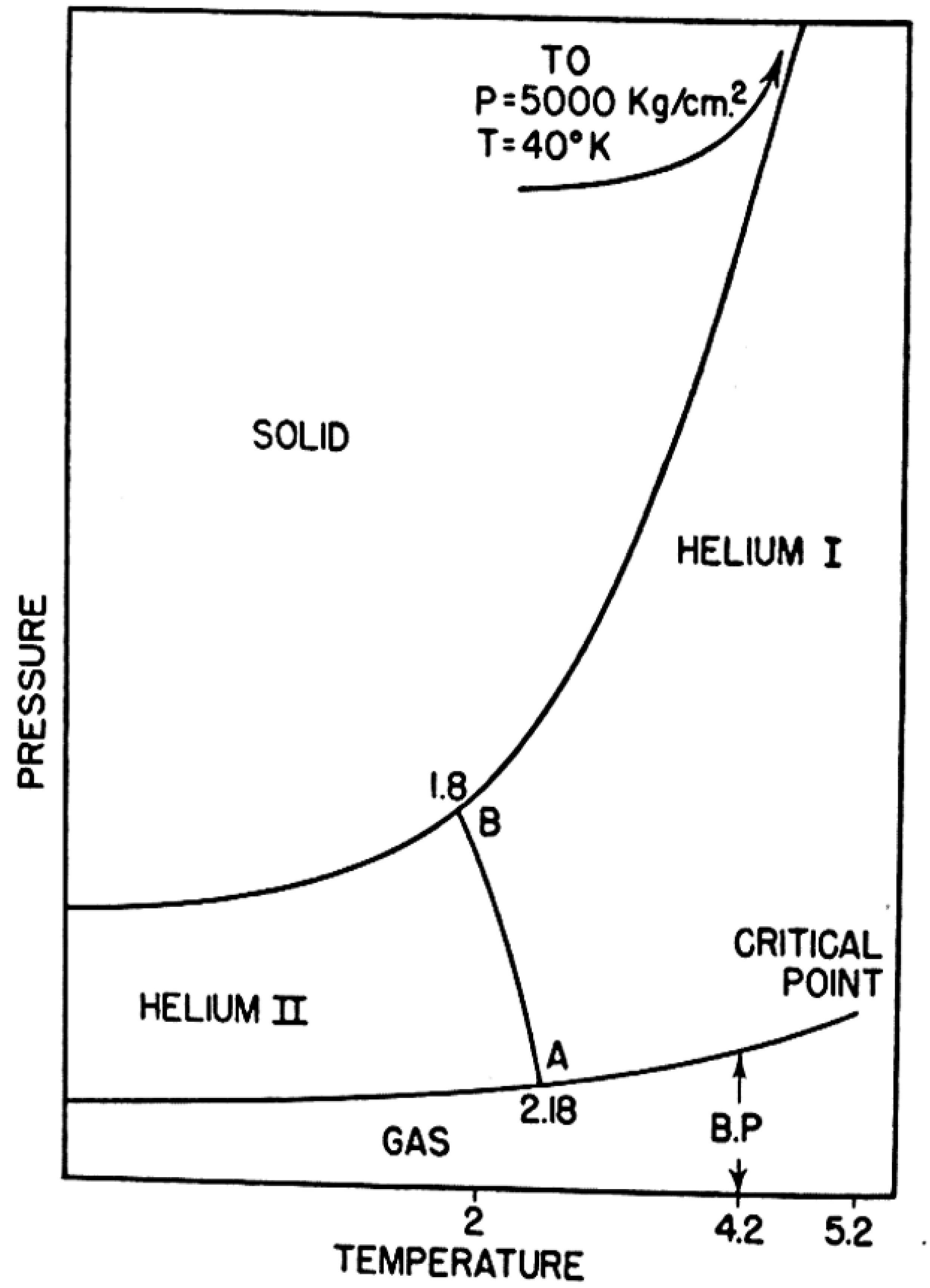

FIG. 105. Phase diagram for helium at very low temperatures, condensed at higher temperatures to show critical point.

QUESTIONS AND PROBLEMS

1. It takes 538.6 cal. to convert 1 gm. of water at 100° C. into vapor at 100° C. under a pressure of 1 atmosphere. The volume of 1 gm. of steam is 1,671 cm.^{3}. How much greater is the energy content of the steam than that of the water?

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[42] W. H. Keesom, A. P. Keesom, and B. F. Saris, *Physica*, **5**, 281 (1938).

[43] W. H. Keesom and G. E. MacWood, *Physica*, **5**, 737 (1938).

2. The specific heats of liquid and solid tin at the melting point (232° C.) are 0.0608 and 0.0595 cal. per gm. per deg. C., respectively. The atomic weight is 119. How many degrees of freedom are associated with the liquid and solid phases by classical theory? What would be the expected value for the heat of fusion, assuming no change in volume on melting?

3. On a certain day when the thermometer reads 28° C., the dew-point temperature is found to be 18° C. What is the relative humidity?

4. From Trouton's rule and assumed data for water, what would you infer regarding the heat of vaporization of iron (B. P. 2,450° C.)?

5. A sealed glass tube contains carbon dioxide in liquid and vapor forms. The temperature is raised until the meniscus is observed to disappear. Does this temperature of disappearance necessarily yield the critical temperature? Explain.

6. Carbon dioxide is stored in a tank at a temperature of 25° C. with a pressure of 100 atmospheres. In what state does it exist in the tank? Tell what happens when the valve is opened. Explain the formation of carbon dioxide snow by reference to a *P–T* diagram. Is it necessary to invert the tank?

7. The melting point of carbon dioxide is given in handbooks as $-57°$ C., and the boiling point is $-78.5°$ C. Discuss the possibility of a substance having a boiling point at a lower temperature than the melting point.

8. Discuss the " reduced " equation of state and show how it is possible to calculate the boiling point of a substance in terms of its critical constants when the complete vapor tension curve of some other substance is known. Follow through some particular case.

9. When the dew-point is 12° C., what is the mass of the water vapor in a room 3 meters by 5 meters by 5 meters, at a temperature of 25° C.?

10. The vapor tension of molybdenum at 2,000° C. is 6.3×10^{-7} mm. of mercury. How much time would be required to reduce a 50-mil (thousandths of an inch) filament, heated to this temperature, to a diameter of 49 mils?

11. Liquid air boils at $-195°$ C., yet a liter Dewar flask filled and left open in a room at 25° C. may still have some liquid remaining after a few days. Explain this phenomenon. What is the end product? How much heat is transferred?

CHAPTER VIII

THERMODYNAMICS — ELEMENTARY

General Considerations. By starting with certain general assumptions it is possible to build up relationships between physical quantities whose interdependence might not otherwise have been suspected. Of these assumptions, certain ones are held inviolable as laws governing the operation of the universe, whereas others are known to be only convenient approximations of the real facts. Of the former type are the first and second laws of thermodynamics. Of the latter type are the ideal properties assumed to be valid for an imaginary material called the " working substance."

The First Law of Thermodynamics. The first law of thermodynamics has already been formulated in Chapter VI, as the application of the law of conservation of energy to transformations of mechanical energy into heat, or vice versa. When a quantity dQ of heat is added to a body a part of it may reside there in the form of increased kinetic energy of the component particles. Another part may exist as increased potential energy of the system of particles if expansion has taken place. The first of these portions of dQ is represented by the symbol dU and is called the change in the internal energy of the system. While the alteration is occurring in the internal energy, it may be that the substance is doing an amount of external work dW. This may be of various forms such as work done against surface tension if the surface is enlarged, or against an external pressure if the volume is enlarged by ΔV, or, in certain cases, against electric or magnetic forces. In the present consideration, only work against an external pressure P will be treated, and this will be regarded as positive if done by the substance, and expressed as PdV. If C_v is the specific heat under a constant volume, then

$$dQ = dU + dW = C_v\,dT + P\,dV \tag{1}$$

are all equivalent forms for expressing the same energy. The quantities dQ and dW are not exact differentials. They are often represented by some distinctive symbol to indicate this property, as opposed to dU which is an exact differential. With this in mind no special symbol will be employed to represent them subsequently.

Second Law of Thermodynamics. This important law may be formally stated as follows: Heat will not of itself flow from one body to another body maintained at a higher temperature. From this we shall see that certain corollaries follow, giving alternative modes of expression. One of these is that no self-acting machine will continuously deliver work at the expense of the energy in the coolest body in the system. No violations of this law have ever been discovered.

Assumptions. *Specific Heat Constant.* In the following discussion, wherever the specific heat of the working substance is concerned, it will be assumed that this quantity is a constant at all temperatures.

Gas Law. The working substance will be considered obedient to the fundamental gas law $PV = RT$ unless otherwise mentioned.

Joule's Law. In 1850 an experiment was carried out by Joule, using an apparatus as shown in Fig. 106. The purpose of this experiment was to observe whether the internal energy of a given mass of gas varied with the volume occupied by the gas. The chamber A was filled with a compressed gas while chamber B was evacuated. The turning of the stopcocks connecting the two chambers allowed the free expansion of the gas into the evacuated chamber. The complete assembly was immersed in a water bath. Now if in the enlarged volume the internal energy had increased or decreased, a corresponding lowering or raising of the temperature of the bath would have been expected. No change in temperature being observed, it was concluded that the internal energy of the gas was a function of its temperature only. This statement is known as Joule's law or sometimes Mayer's hypothesis. It is known that the failure to observe a variation in temperature was due to a lack of sensitivity of the apparatus. Joule and Thomson in their famous porous plug experiments, described later on page 244, used a continuously expanding gas and showed that the internal energy at a given temperature was also a function of the volume occupied. In the following discussion it will be assumed that the working substance obeys Joule's law.

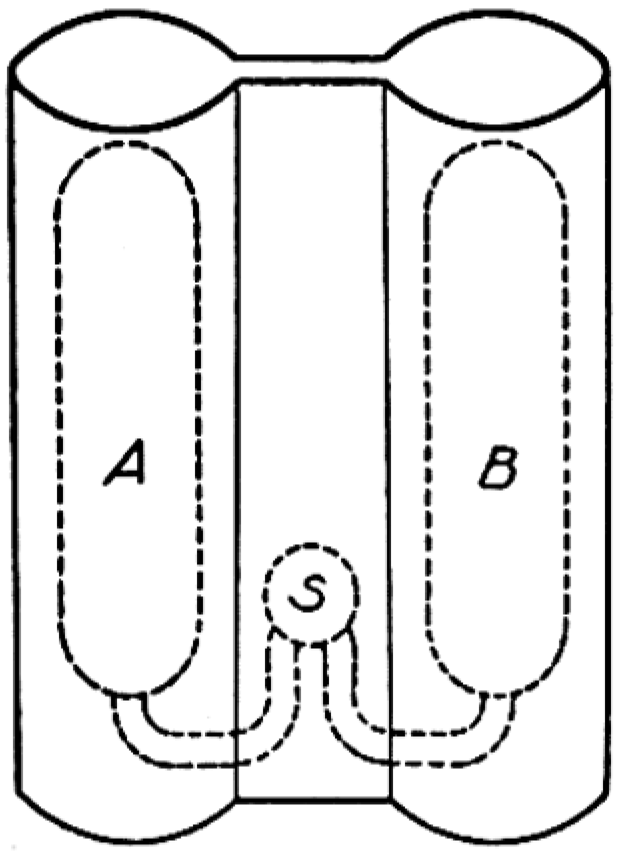

FIG. 106. Apparatus of Joule to study the free expansion of a gas.

Principle of Maximum Work. If a mass m be added to a weight pan which is at rest and supported by a coiled spring, then when the system again comes to rest the increased potential energy of the spring will be only one-half of the loss in potential energy of the mass m. If the mass had been added in infinitesimal increments, then the loss in potential energy of the mass would have been entirely stored in the spring in increased potential energy. Similarly, a compressed gas has ability to do external work. If the pressure to which it is subjected is reduced in infinitesimal steps, the gas will expand, doing a maximum amount of work. In all expansions and compressions to be considered it will be assumed that only infinitesimal differences in pressure exist.

Carnot Cycle. In 1824 there was published[1] by Sadi Carnot an important treatise entitled *The Motive Power of Heat.* Although at that time the possibility of obtaining work from heat energy was well known, as evidenced by the use of the steam engine, the general laws governing the efficiency of the operation were not understood. By imagining a definite amount of working substance allowed to expand and to do external work, and then subsequently to be restored to its initial condition, one is in a position to reason regarding external processes and their equivalence. This operation may be termed " taking the substance about a cycle."

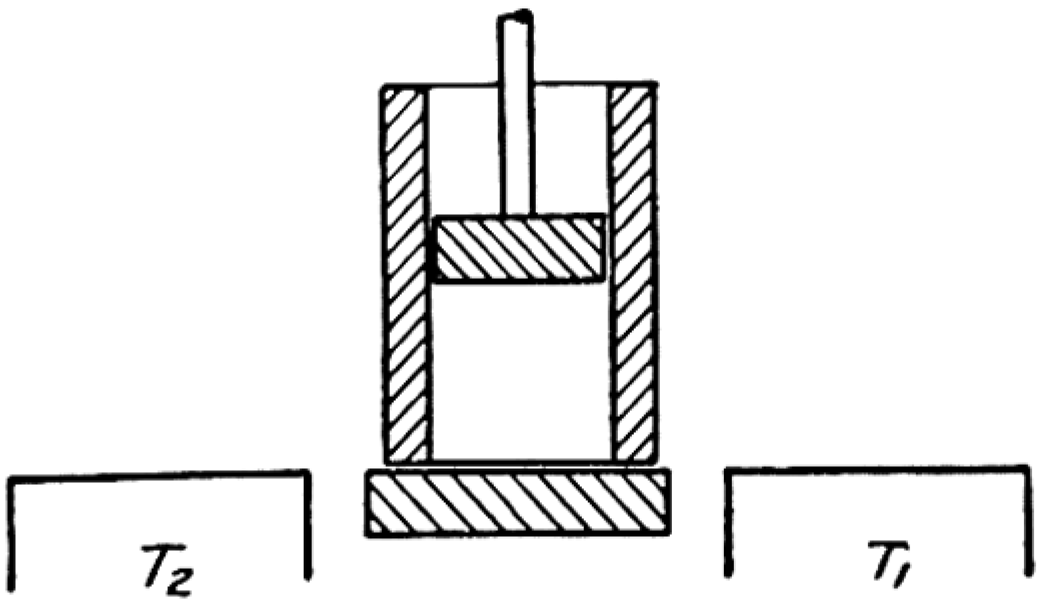

FIG. 107. Schematic view of a Carnot engine as proposed by Clapeyron.

The mechanism for picturing such a cycle as proposed by Clapeyron is shown in Fig. 107. This consists of a cylinder with thermally insulated walls and piston, containing a definite amount of " working substance." By a mere sliding of the cylinder it may be changed from a condition of good thermal contact with a source at a high temperature T_1, to an insulating base or in turn to a reservoir at a low temperature T_2. The cycle imagined by Carnot is shown in Fig. 108. This geometric representation was first offered by Clapeyron,[2] who, it appears, was the first to recognize the merit in Carnot's publication ten years earlier.

In this cycle, the working substance at a volume V_1 and temperature T_1 is placed in contact with the source at a high temperature T_1. Now, decreasing the pressure by infinitesimal steps, the volume increases isothermally, since the thermal capacity of the cylinder is regarded as very small compared to that of the reservoir. At a certain volume V_2 the cylinder is moved to the insulating base. A continued decrease in the external pressure is accompanied by an increase in the volume but now along an adiabatic line, since no transfer of heat is allowed. This process is continued until the temperature of the working substance has fallen to that of the reservoir at the low temperature T_2. At this instant the cylinder is moved into a position of good thermal contact with this reservoir. The external pressure is now increased by infinitesimal steps and the volume decreases isothermally. When a volume V_4 as shown by the point D is reached, such that the adiabatic passing through it also passes through A, the isothermal compression is stopped and the cylinder replaced upon the insulating base. It is now subjected to an adiabatic compression bringing the working substance back to the initial condition.

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[1] S. Carnot, *Réflexions sur la puissance motrice du feu*, 1824.

[2] E. Clapeyron, *École Polyt. Jour.*, **14**, 153 (1834).

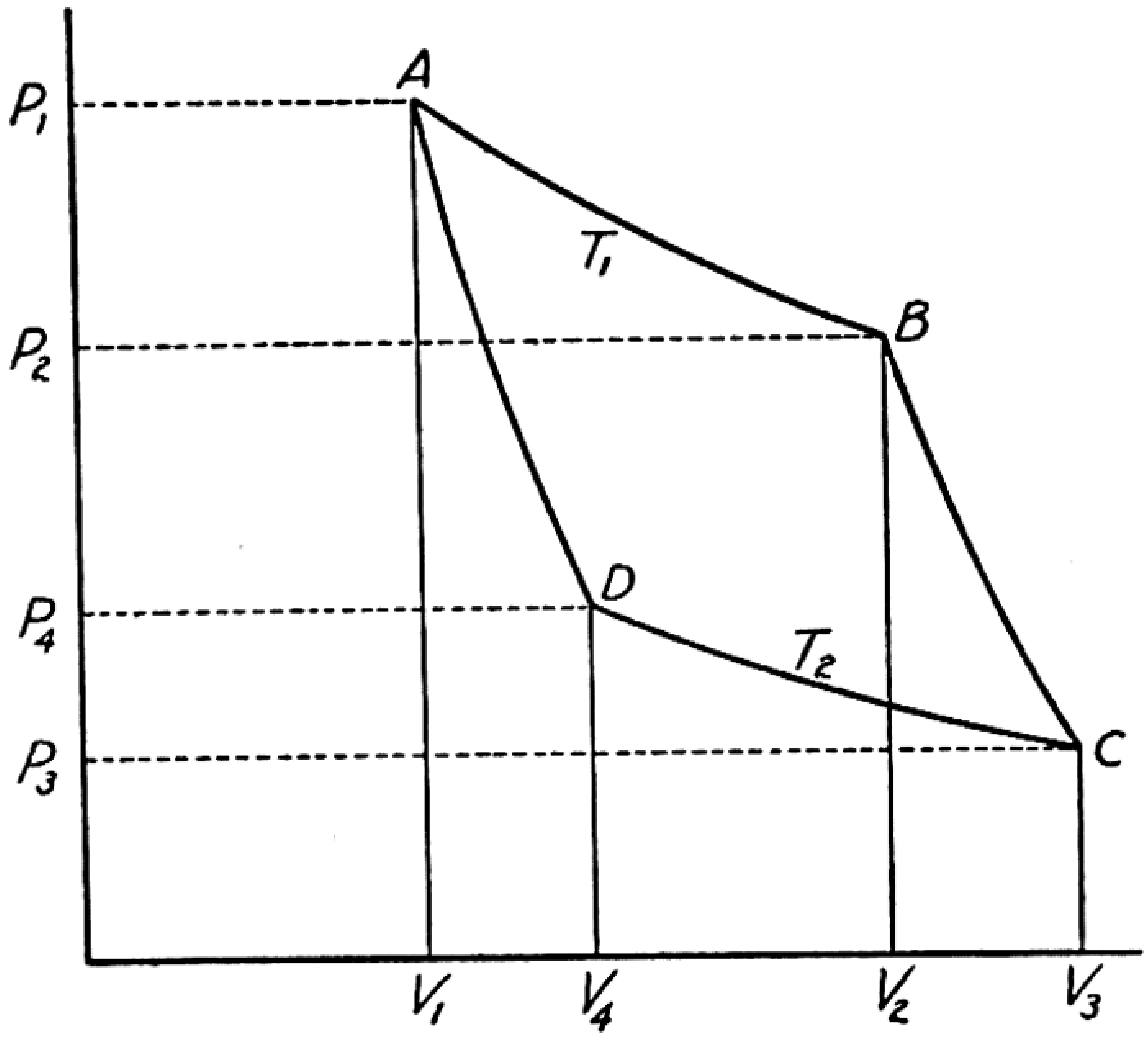

FIG. 108. The cycle of Carnot on a pressure versus volume plot.

If in this process the piston is frictionless and all changes have taken place with sufficient slowness to avoid the development of kinetic energy in any part of the system, and if moreover all transfers of heat have taken place under infinitesimal temperature gradients, then the process is reversible. This means that it is possible to go about the cycle in the reverse direction and abstract heat, where before it was absorbed, and do work upon the system where previously work was done by the system and restore the original conditions.

From A to B a quantity of heat Q_1 is taken in by the working substance and a quantity of work W_1 equal to $\int_{V_1}^{V_2} P \cdot dV$ is done. This work is geometrically the area under the curve AB. By Joule's law the internal energy at B is the same as at A since the temperature is the same, so that $Q_1 = W_1$. The work done from B to C, being the area under the curve or $\int_{V_2}^{V_3} P \cdot dV$ where P obeys the adiabatic relationship of equation 31 in Chapter IV, may be represented as W_2. Similarly from C to D during the isothermal compression, a quantity of heat Q_2 is passed into the condenser at the expense of an amount of work done upon the system. This work is denoted in magnitude by W_3 and is regarded as negative in sign and hence is equal to $-\int_{V_4}^{V_3} P \cdot dV$. From D to A during the adiabatic compression an additional amount of work W_4 equal to $-\int_{V_1}^{V_4} P \cdot dV$ is done upon the system.

Now, by definition, the efficiency of the machine $\left(\frac{\text{Work output}}{\text{Energy input}}\right)$ becomes

$$\text{Eff.} = \frac{Q_1 + W_2 - Q_2 - W_4}{Q_1} \tag{2}$$

But W_2 may be shown to be equal to W_4 if the working substance be assumed an ideal gas. Making use of the adiabatic relationship developed on page 55 ($PV^\gamma = P_2V_2^\gamma = P_3V_3^\gamma$), then

$$W_2 = \int_{V_2}^{V_3} P \cdot dV = \int_{V_2}^{V_3} P_2V_2^\gamma \cdot \frac{dV}{V^\gamma} = \frac{P_2V_2^\gamma}{1-\gamma}\left[V^{1-\gamma}\right]_{V_2}^{V_3}$$
$$= \frac{P_3V_3 - P_2V_2}{1-\gamma} \tag{3}$$

Similarly:

$$W_4 = \frac{P_4V_4 - P_1V_1}{1-\gamma} \tag{4}$$

But $P_1V_1 = P_2V_2$, and $P_3V_3 = P_4V_4$, so that $W_2 = W_4$. Hence the efficiency becomes

$$\text{Eff.} = \frac{Q_1 - Q_2}{Q_1} = \frac{\int_{V_1}^{V_2} P \cdot dV - \int_{V_4}^{V_3} P \cdot dV}{\int_{V_1}^{V_2} PdV} \tag{5}$$

But from the universal gas law $PV = RT$, so that P may be replaced by RT/V, giving

$$\text{Eff.} = \frac{RT_1 \int_{V_1}^{V_2} \frac{dV}{V} - RT_2 \int_{V_4}^{V_3} \frac{dV}{V}}{RT_1 \int_{V_1}^{V_2} \frac{dV}{V}}$$

$$= \frac{R\left[T_1 \log \frac{V_2}{V_1} - T_2 \log \frac{V_3}{V_4}\right]}{RT_1 \log \frac{V_2}{V_1}} \tag{6}$$

Now V_2/V_1 may be shown to be equal to V_3/V_4. This leads to the final expression for the efficiency,

$$\text{Efficiency} = \frac{T_1 - T_2}{T_1} \tag{7}$$

This relationship between the volumes follows from the equations relating the isothermal and the adiabatic states. Thus

$$\text{(Isothermal)} \quad P_1V_1 = P_2V_2 \tag{8}$$

and

$$P_3V_3 = P_4V_4 \tag{9}$$

$$\text{(Adiabatic)} \quad P_1V_1^\gamma = P_4V_4^\gamma \tag{10}$$

and

$$P_3V_3^\gamma = P_2V_2^\gamma \tag{11}$$

On dividing equation 8 by equation 10 and equation 9 by equation 11 the following are obtained:

$$\frac{V_1}{V_1^\gamma} = \frac{P_2V_2}{P_4V_4^\gamma} \tag{12}$$

and

$$\frac{V_3}{V_3^\gamma} = \frac{P_4V_4}{P_2V_2^\gamma} \tag{13}$$

Multiplying equation 12 by equation 13 and taking the $(\gamma - 1)$ root gives the desired result:

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \tag{14}$$

Efficiency of Reversible Engine, Single Valued. Although in the above development the working substance was assumed to be an ideal gas, any other reversible cycle that might be imagined to work between the same temperatures must have resulted in the same value for the efficiency. To establish this fact it is only necessary to assume the existence of an engine with an efficiency E greater than the efficiency E' of the reversible engine considered. A connection is made between the two engines so that the reversible engine with the lesser imagined efficiency, E', works backward, i.e., absorbs heat Q_0' from the condenser, receives external work, W', and passes a quantity of heat, Q', to the source at the high temperature, T, while the engine with the higher efficiency E works forward. By adjusting the dimensions of the cylinder, the work done by the one engine may be made equal to that done upon the other system. The schematic arrangement is shown in Fig. 109. The hotter body at the temperature T is shown at the top and the body at the lower temperature T_0 is at the bottom.

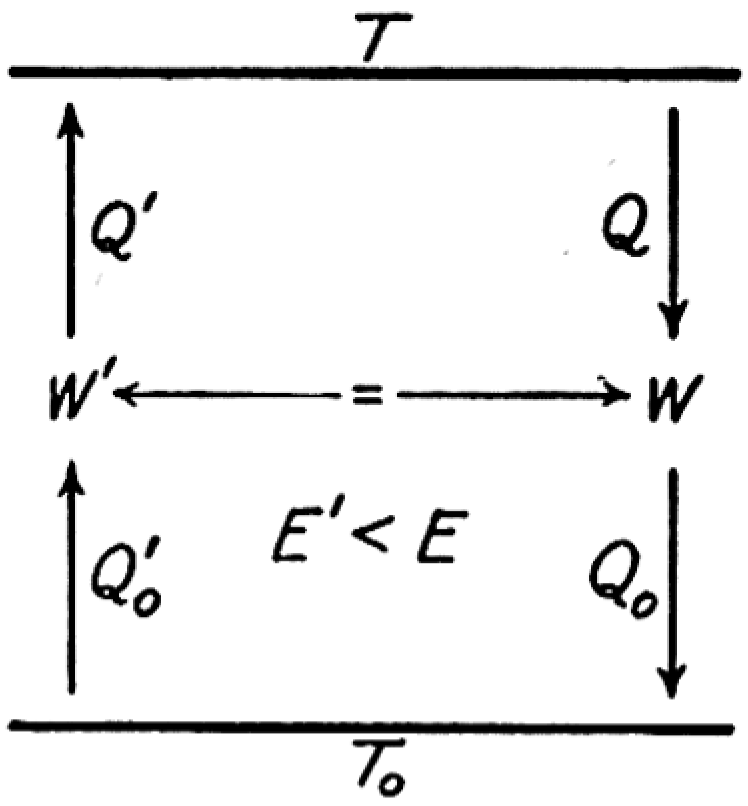

FIG. 109. Schematic representation of heat flow for a reversible engine coupled to another of greater imagined efficiency.

$$\text{Eff. } E' = \frac{W'}{Q'} = \frac{Q' - Q_0'}{Q'} < E = \frac{W}{Q} = \frac{Q - Q_0}{Q} \tag{15}$$

But $W = W'$. Hence $Q' > Q$ and also $Q_0' > Q_0$.

This process does not violate the first law of thermodynamics. It would, however, result in a continuous transfer of heat from the colder body to the warmer of $(Q_0' - Q_0)$ per cycle. This result is a violation of the second law of thermodynamics and therefore is just as effectively forbidden.

Practical Engine Cycles. (*a*) *Reciprocating Steam Engine.* A graph showing the relationship between the pressure and the volume for the reciprocating steam engine is shown in Fig. 110. The enclosed area in the figure is proportional to the work done in the cycle, and the graph is often termed an indicator diagram. From A to B the intake valve is open and expansion occurs under approximately constant pressure, since the volume of the engine cylinder is small compared with the volume of the boiler. At B the intake valve closes and from B to C the expansion is practically adiabatic. Actually P falls more rapidly than for an adiabatic on account of the loss in heat through the walls of the cylinder. At C the exhaust valve opens and the pressure drops to that of the condenser as shown by D. During the next step the volume decreases, expelling any vapor residue at constant pressure. This is shown by the line D to E. The exhaust valve now closes and the inlet valve opens, restoring the initial condition. Unlike the Carnot engine the mass of material in this cycle is, of course, not constant. In practice the system is in motion while the valves are operating so that all ideally sharp corners are rounded off as a result.

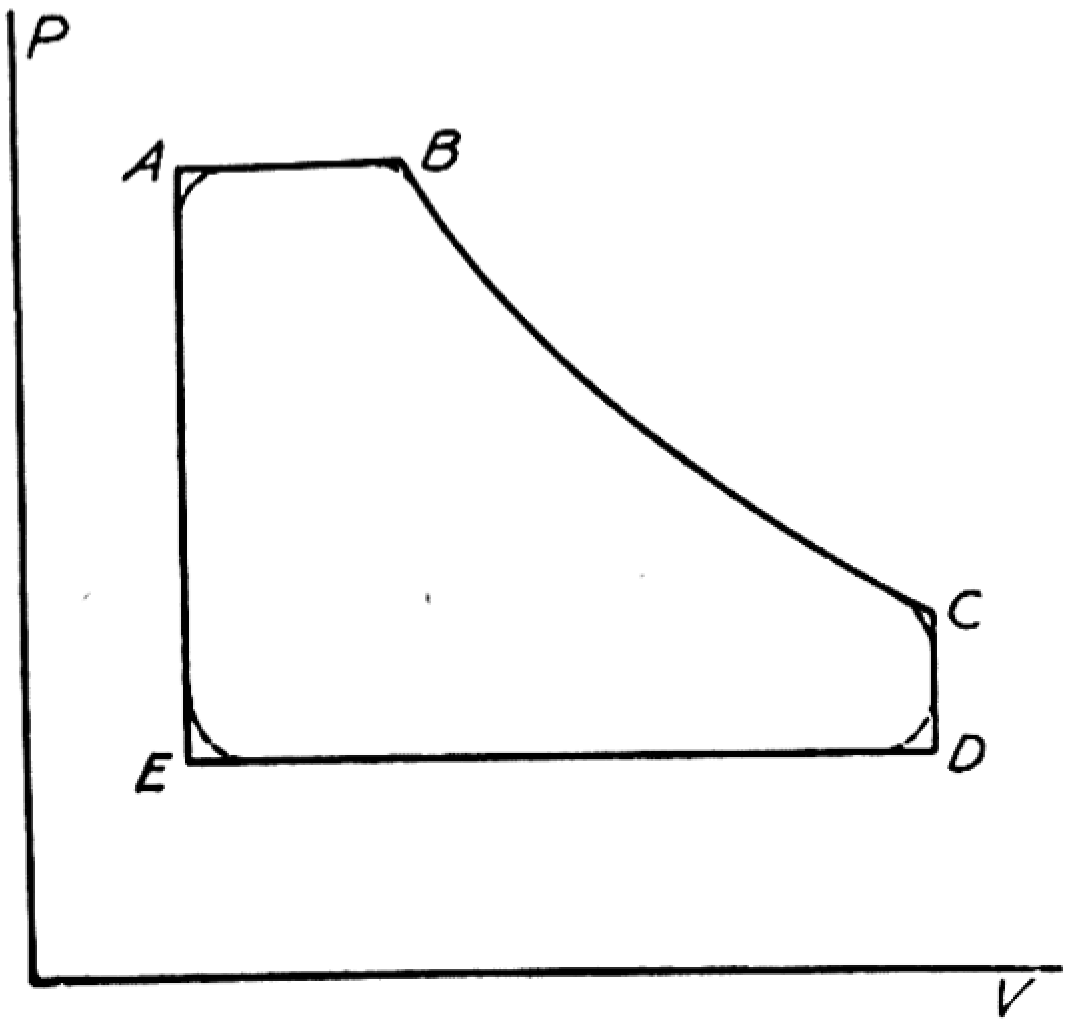

FIG. 110. Pressure and volume relationship in a reciprocating steam engine.

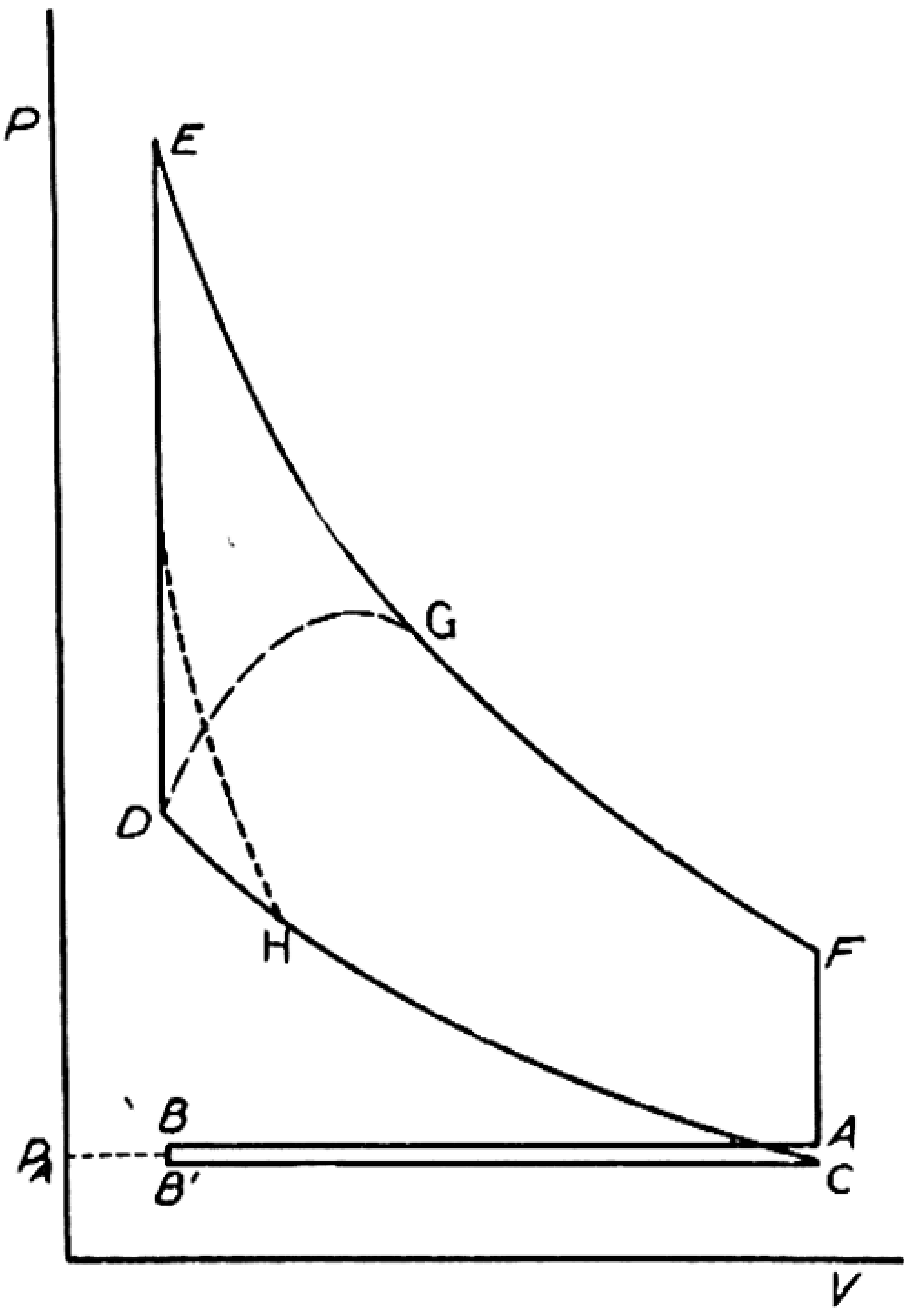

FIG. 111. Diagram representing the action of a four-cycle gas engine.

(*b*) *Four-Cycle Gas Engine.* The indicator diagram of a four-cycle gas engine is shown in Fig. 111. Starting at C with the cylinder full of fuel gas, the inlet valve closes and a compression, ideally adiabatic as shown by CD, ensues. Actually, owing to the cooling or heating effects of the walls of the cylinder, this may be either steeper or less steep than an adiabatic. At D, ideally, the explosion occurs instantaneously increasing the pressure enormously to a value shown by E. This is followed by an adiabatic expansion to F when the exhaust valve opens and the pressure drops to A. At a pressure slightly greater than atmospheric, the waste gases are expelled as shown by AB. The exhaust valve now closes and the inlet valve opens. At a pressure less than atmospheric, the vaporized fuel is drawn into the cylinder as shown by the line $B'C$, bringing conditions back to those of the starting point. In practice some time is required for the propagation of the flame throughout the cylinder during the explosion so that the pressure *DE* is built up in a finite time. During this time the motion of the cylinder may have increased the volume so that the line *DG* represents the actual pressure developed. By advancing the firing position to *H*, a pressure formation shown by the portion of the curve *H* to *E* may occur. In this case the area representing the output work is only slightly less than the ideal value, whereas if firing starts at *D* a very large portion of the area is cut off.

Kelvin Scale of Temperature. The fact that a reversible engine working between any two temperatures has an efficiency entirely independent of any particular physical property of the working substance led Lord Kelvin[3] to suggest this as the basis of a fundamental scale of temperature. In this, two temperatures would be taken as proportional to the quantities of heat absorbed and ejected by a reversible engine working cyclically between them. By adopting two fixed points as in all other scales of temperature, such as the freezing point and the boiling point of pure water, corresponding numbers could be affixed at other temperatures. The zero of this scale would be of necessity the absolute zero, since a condenser maintained at this temperature would receive no heat and the cycle would have an efficiency of unity.

For an ideal gas as the working substance, executing a reversible cycle, we have seen in equation 7 that if Q_1 is the quantity of heat received at the temperature T_1 and Q_2 is the quantity of heat ejected at the temperature T_2, then

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{16}$$

These temperatures in equation 16 are measured on the gas thermometer. Equation 16 may be rewritten as

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \tag{17}$$

from which it follows that

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1} \tag{18}$$

This statement is identical with the assumption of Kelvin regarding absolute thermodynamic temperatures. Actual gases have been shown to deviate from the ideal gas law, and to that extent temperatures measured by the gas thermometer differ from the absolute Kelvin values. Knowing the constants in the equation of van der Waals for the gas that is used in the thermometer it is possible to compute the slight alterations that are necessary to change the observed gas temperatures to their corresponding thermodynamic values. Such information may be obtained by observing either (*a*) the deviation of the gas from Boyle's law or (*b*) the cooling or heating effect as the gas is allowed to expand through a nozzle as in the experiment of the porous plug.

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[3] W. Thomson, *Phil. Mag.*, **33**, 313 (1848).

Such corrections have been made by Callendar[4] for a few gases from information of the latter type, assuming the scales to agree at 0° C. More recently, calculations based upon the behavior of a gas upon compression have been carried out at Leiden[5] and in Berlin[6] by various investigators. A summary of the recent work on several gases has been presented by F. G. Keyes[7] together with data on helium, air, and nitrogen, by J. R. Roebuck[8] and T. Murrell. The agreement between these calculations is illustrated in Table 16 which shows for hydrogen at a few temperatures the correction to be added to the observed temperature to convert it to the thermodynamic or Kelvin value.

TABLE 16

OBSERVED AND THERMODYNAMIC TEMPERATURES FOR HYDROGEN

Kelvin Temperature Equals T + Correction

T° C.	Correction as Calculated by		
	Callendar	Keesom and Tuyn	Keyes
+200	+0.00236	....	+0.0071
150	0.00097	....	....
100	0	0	0
50	−0.00040	....	....
0	0	0	0
− 50	+0.00164	+0.002	+0.0037
−100	0.0054	0.009	0.0108
−150	0.0132	0.022	0.0230
−200	0.0311	0.046	0.0436
−250	0.1005	0.100	0.0888

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[4] H. L. Callendar, *Phil. Mag.*, **5**, 48 (1903).

[5] P. G. Cath and H. Kammerlingh Onnes, *Comm. Phys. Lab.*, Leiden, **156** (1922); W. H. Keesom and W. van Tuyn, *Comm. Phys. Lab. Supplement*, 78, 1936.

[6] L. Holborn and J. Otto, *Zeit. Phys.*, **30**, 320 (1924); **33**, 11 (1925); **38**, 359 (1926); F. Henning, *Trav. mem. Bur. Int. des Poids et Més*, 1938.

[7] F. G. Keyes, *Temperature, Amer. Inst. Phys.*, p. 45, Reinhold Publishing Corp. 1941.

[8] J. R. Roebuck and T. A. Murrell, *Temperature, Amer. Inst. Phys.*, p. 60, Reinhold Publishing Corp., 1941.

The Reversible Cycle as Heating Agent. For values of T_2 considerably above the absolute zero the value of the efficiency in equation 7 is low, even for the ideal process. In actual processes where the intake temperature T_1 is much less than the temperature of combustion the efficiency is still further reduced. Now let the cycle be considered as applied to a refrigerating system (i.e., worked backward so that the working substance at the colder temperature T_2 absorbs a quantity of heat Q_2 and has done upon it an amount of work W and ejects to the reservoir at the higher temperature T_1 a quantity of heat Q_1). Then equation 17 gives

$$Q_1 = \frac{T_1}{T_1 - T_2} \cdot W \tag{19}$$

Thus the heat communicated to the body at the high temperature may be many times the value of the work done. The application of this to the practical problem of heating was suggested by Lord Kelvin.[9] Its practicability is of course dependent upon the efficiency with which the energy of combustion may be first transformed into mechanical work. Modern refrigerators are able to extract more than twice as much energy from the cold body than is required to operate the compressor. In this sense they may be said to have an efficiency greater than 200 per cent.

Exact Differentials. If the quantity U is a function of two independent variables x and y, then the differential of U may be written

$$dU = \frac{\partial U}{\partial x} \cdot dx + \frac{\partial U}{\partial y} \cdot dy = L\,dx + M\,dy \tag{20}$$

Since the order of differentiation is not important it follows that

$$\left(\frac{\partial L}{\partial y}\right)_{x=\text{const.}} = \left(\frac{\partial M}{\partial x}\right)_{y=\text{const.}} \tag{21}$$

The quantity $L\,dx + M\,dy$ is called an *exact* differential since it is precisely the differential of some function U. The importance of knowing the nature of the differential lies in the fact that, if the variation in a quantity may be represented by an exact differential, then the change in that quantity is determined entirely by the initial and final conditions and not at all by the type of transformation connecting the two states. Thus the change in the internal energy may be represented by an exact differential, since by Joule's law for a given amount of substance the internal energy is uniquely determined by the temperature. The increment of work indicated in equation 1 is not an exact differential since it obviously is dependent upon the type of expansion occurring during the process. Differential expressions which are not exact may often be rendered so by multiplying them by a factor. Thus $xdy - ydx$ is not an exact differential of any quantity but by multiplying it by $1/x^2$, $1/y^2$, or $1/xy$, etc., the expression satisfies the above relationship and becomes an exact differential. These multiplying factors are called integrating factors.

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[9] W. Thomson, *Glas. Phys. Soc. Proc.*, **3**, 269 (1848).

Entropy. Although equation 1 is not, as it stands, an exact differential, it may be made one by the application of an integrating factor $1/T$. Thus

$$\begin{aligned}\frac{dQ}{T} &= \frac{dU}{T} + \frac{PdV}{T} = C_v\frac{dT}{T} + R\frac{dV}{V} \\ &= d[C_v \log T + R \log V] = d\phi \qquad (22)\end{aligned}$$

By definition, this quantity ϕ whose variation is represented by this exact differential is termed the *entropy* of the substance. It is apparent that this quantity characteristic of a body increases when heat is added to the body and decreases when heat is subtracted. Its total change for a reversible process is consequently expressed as

$$\phi_2 - \phi_1 = \int_0^Q \frac{dQ}{T} \qquad (23)$$

Like energy, the absolute value of entropy is unknown; only changes in its value may be determined. An arbitrary zero may be assumed.

During a reversible adiabatic process the entropy is constant. The graphical locus of the points representing this condition is termed an isentropic line. Using entropy in conjunction with temperature as coordinates the area representing the work done in the cycle of Carnot becomes rectangular in form as shown in Fig. 112.

In the reversible cycle of Carnot we have seen that $Q_1/T_1 = Q_2/T_2$, or the net gain in entropy of the whole system is zero. This is not true, however, in all actual processes. For example, for the isothermal expansion A to B the source loses a quantity of heat Q_1 at a temperature T_1, and this same quantity of heat arrives at the working substance, actually at a lower temperature. Thus, more entropy is gained by the working substance than is lost by the source. Likewise from C to D more entropy is gained by the condenser than is lost by the working substance. Hence, for the system as a whole, the entropy increases with time. The statement that all natural processes proceed in such a way that the entropy of the system approaches a maximum value may be regarded as an alternative statement of the second law of thermodynamics.

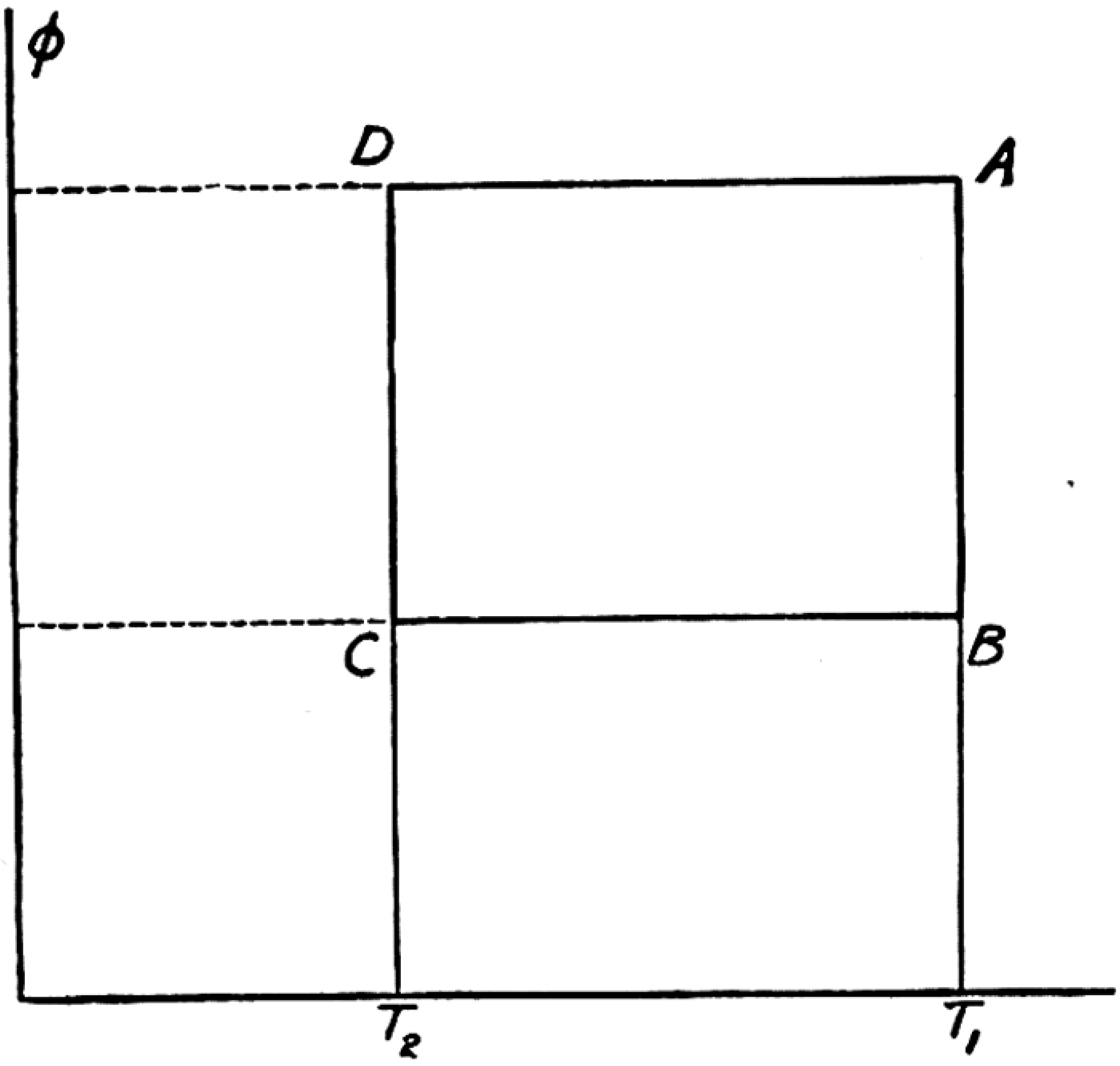

FIG. 112. The Carnot cycle on a plot of entropy versus temperature.

Entropy and Probability. From equation 22, in which

$$d\phi = C_v \frac{dT}{T} + R\frac{dV}{V}$$

it follows by integration that

$$\phi = C_v \log T + R \log V + C \tag{24}$$

The constant C is thus the value of the entropy for $T = 1$ and $V = 1$.

Since all natural processes proceed toward a condition of maximum entropy and since the velocities of the constituent particles approach the most probable distribution, there must be an intimate relationship between the entropy of the substance and the probability of a particular distribution.

This subject was originally treated by Boltzmann.[10] The term " distribution of velocities " might mean the complete definition of velocity (magnitude and direction) of every individual molecule. This picture at any instant was called an *arrangement*. On the other hand, the term might simply refer to the number of molecules in each particular interval of velocity v to $v + dv$ without regard to the direction or identity of the particles. This is called a *complexion*. For a definite number of particles possessing in total a given amount of energy there exists a number of complexions. This corresponds in Fig. 24 to the possibility of a number of other forms of the curve, all having the same area. For each complexion a great number of arrangements are possible. The most probable complexion is that one having the greatest number of possible arrangements. Now assuming in the simplest case that the particles were elastic spheres, and properly choosing the constant of integration, Boltzmann was led to the following relationship between entropy and probability

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[10] L. Boltzmann, *Vorlesungen über Gastheorie*, vol. 1, 1896.

$$\phi = a \log P \tag{25}$$

where P represents the probability of the complexion of the gas, and a is a constant.

The Four Thermodynamic Relationships. When two independent equations are established between any number of variables characteristic of a substance it is possible to deduce other relationships among the variables, not themselves evident. These deduced relationships make it possible to evaluate certain quantities not readily measurable, in terms of other known quantities. Four such deduced equations known as Maxwell's four thermodynamic formulae will be developed.

The quantity dU is, from Joule's law, an exact differential,

$$dU = dQ - PdV = T \cdot d\phi - P \cdot dV \tag{26}$$

Also,

$$d(PV) = P \cdot dV + V \cdot dP \tag{27}$$

The differential of the sum or difference of two quantities is an exact differential provided the differential of each quantity is exact. So that

$$d(U + PV) = T \cdot d\phi + V \cdot dP \tag{28}$$

is an exact differential. This quantity $U + PV$ has been called the " total heat " or the enthalpy of the substance and is often denoted by the single symbol H.

Similarly, on writing

$$d(T\phi) = T \cdot d\phi + \phi \cdot dT \tag{29}$$

the following exact differential may be formed:

$$d(U - T\phi) = P \cdot dV - \phi \cdot dT \tag{30}$$

The quantity $(U - T\phi)$ has been called the " free energy " or the " available energy " and is usually denoted by the single symbol F. From equations 28 and 29 the following exact differential may be formed:

$$d(U + PV - T\phi) = V \cdot dP - \phi \cdot dT \tag{31}$$

The quantity $U + PV - T\phi$ has been called "the thermodynamic potential at constant pressure" or more commonly the "Gibbs function," and is represented by the single symbol G.

By equating the differentials of the coefficients of equations 26, 28, 30, and 31, the four fundamental thermodynamic equations follow:

$$\left(\frac{\partial T}{\partial V}\right)_\phi = -\left(\frac{\partial P}{\partial \phi}\right)_V = -T\left(\frac{\partial P}{\partial Q}\right)_V \tag{32}$$

$$\left(\frac{\partial T}{\partial P}\right)_\phi = \left(\frac{\partial V}{\partial \phi}\right)_P = T\left(\frac{\partial V}{\partial Q}\right)_P \tag{33}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial \phi}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial Q}{\partial V}\right)_T \tag{34}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial \phi}{\partial P}\right)_T = -\frac{1}{T}\left(\frac{\partial Q}{\partial P}\right)_T \tag{35}$$

The physical interpretation of these relationships is at once apparent. As an illustration of the application of the equations let us consider equation 34. This important relationship is often called the Clapeyron-Clausius equation. From the right-hand member we see that heat dQ is added to a body at the constant temperature T. With no change in temperature, the added heat must therefore produce a change in state. Hence this equation is applicable to processes involving a change of state such as sublimation, boiling, and melting. The left-hand member has to do with the change in pressure per unit change of temperature. This may mean the slope of either the vapor-tension curve or the sublimation or frost line or the melting-point curve. The single equation may be solved for one unknown. This may be chosen to be the slope of the vapor-tension curve, the change in the melting point with pressure, the latent heats of fusion, vaporization, or sublimation, or the density of vapor, liquid, or solid or the transformation temperature. The quantity of heat dQ is generally made equal to the particular latent heat per gram that is pertinent, and dV is then the corresponding difference in the specific volume for the two phases concerned. The following applications will be considered.

Change in Melting Point with Pressure. For a substance which expands upon melting, $(\partial\phi/\partial V)_T$ is positive. Hence it follows that $(\partial P/\partial T)_V$ is also positive or an increased pressure raises the melting point as shown by curve b, Fig. 81. The change in pressure that is needed to produce a unit change in the melting point follows.

$$\begin{aligned}\frac{dP}{dT} &= \frac{L_{S\rightarrow L}}{T(V_L - V_S)}\\ &= \text{(for water)}\ \frac{80 \times 4.186 \times 10^7}{273\ (1.00013 - 1.09051)\ (76 \times 13.6 \times 980)}\\ &= -\ 135.8\ \frac{\text{atm.}}{\text{deg. C.}}\end{aligned} \tag{36}$$

The subscripts, S and L, are used to denote solid and liquid, respectively.

Frost Line and Vapor-Tension Curve at the Triple Point. In Fig. 88 the sublimation curve at the triple point is represented as having a steeper slope than the vapor-tension curve. The justification of this follows directly from equation 34.

For the vapor-tension curve

$$\frac{dP}{dT} = \frac{L_{L\rightarrow V}}{T(V_V - V_L)} \tag{37}$$

For the sublimation curve

$$\frac{dP}{dT} = \frac{L_{S\rightarrow V}}{T(V_V - V_S)} \tag{38}$$

The denominators of the right-hand members in equations 37 and 38 are almost identical. The numerators, however, are quite different, since at the triple point the heat of sublimation must equal the sum of the heat of fusion and the heat of vaporization; i.e., $L_{S\rightarrow V} = L_{L\rightarrow V} + L_{S\rightarrow L} = 596 + 80$ (for water).

Hence $(\partial P/\partial T)_V$ is greater in equation 38, i.e., for the sublimation curve.

Peltier and Thomson Coefficients. In retrospect many physical processes may be considered from the point of view of these established thermodynamic relationships. The thermoelectric circuit of Seebeck may be regarded as a heat engine. Neglecting the resistance of the wires and assuming an ideal electric motor to replace the potential indicator, then a quantity of heat, Q_1, is absorbed at the hot junction whose temperature is T_1, and a quantity Q_2 is ejected at the cold junction, at a temperature T_2. A quantity of work $(Q_1 - Q_2)$ is developed in the electric motor equal to Ee, where e is the quantity of electricity flowing and E is the potential difference between the terminals. Now a Peltier coefficient π may be defined such that, if a quantity of electricity is made to flow about the circuit in the reverse direction and Q is the quantity of heat absorbed or released at the junction, then

$$\pi = \frac{dQ}{de} \tag{39}$$

(i.e., the Peltier coefficient is the heat liberated per coulomb of electricity transported across the junction). Similarly, this quantity of electricity e flowing in a single conductor between regions at temperatures T_1 and T_2 and releasing or absorbing a quantity of heat Q' allows the definition of a Thomson coefficient τ such that

$$\tau = \frac{1}{T_2 - T_1} \cdot \frac{dQ'}{de} \tag{40}$$

(i.e., the Thomson coefficient is the heat liberated per coulomb of electricity transported per unit difference of temperature). The work that must be done upon this circuit to make the charge e flow about in the reverse direction is then Ee. Now if Q_1 is the Peltier heat ejected at the hot junction, Q_2 that absorbed at the cold junction, Q_1 the Thomson heat given off in one wire, and Q_2' that absorbed in the other, then this same work that is done to make the electric charge e flow about the circuit is

$$\begin{aligned} Ee &= (Q_1 - Q_2)_{\text{Peltier}} + (Q_1' - Q_2')_{\text{Thomson}} \\ &= \pi_1 e - \pi_2 e + \int_{T_2}^{T_1} \tau_1 e \cdot dT - \int_{T_2}^{T_1} \tau_2 e \cdot dT \end{aligned} \tag{41}$$

Here π_1 is the Peltier coefficient at the hot junction whose temperature is T_1, π_2 is the Peltier coefficient at the cold junction whose temperature is T_2, τ_1 is the Thomson coefficient in one wire, and τ_2 is the Thomson coefficient in the second wire. Considering the process to be reversible, then the total change in entropy is zero, so that:

$$\Sigma \frac{dQ}{T} = 0 = \frac{\pi_1 e}{T_1} - \frac{\pi_2 e}{T_2} + e\int_{T_2}^{T_1} \frac{\tau_1 - \tau_2}{T} \cdot dT \tag{42}$$

Differentiating this with respect to T gives

$$\frac{d\left(\frac{\pi}{T}\right)}{dT} + \frac{\tau_1 - \tau_2}{T} = 0 \tag{43}$$

or

$$\tau_1 - \tau_2 = \frac{\pi}{T} - \frac{d\pi}{dT} \tag{44}$$

Combining equations 41 and 44, it follows that

$$E = \pi_1 - \pi_2 + \int_{T_2}^{T_1} \left(\frac{\pi}{T} - \frac{d\pi}{dT}\right) dT = \int_{T_2}^{T_1} \frac{\pi}{T} \cdot dT \tag{45}$$

From this equation the Peltier coefficient may be explicitly expressed as

$$\pi = T\frac{dE}{dT} \tag{46}$$

Differentiating equation 41 with respect to T and rearranging gives for the difference of the two Thomson coefficients

$$\tau_1 - \tau_2 = \frac{dE}{dT} - \frac{d\pi}{dT} = \frac{dE}{dT} - \frac{d\left(T\frac{dE}{dT}\right)}{dT} = -T\frac{d^2E}{dT^2} \tag{47}$$

The Velocity of Sound through Gases. The expression for the velocity of sound through gases as deduced by Laplace[11] is that

$$V = \sqrt{\frac{\gamma P}{\rho}} \tag{48}$$

where P is the pressure, ρ is the density and γ is the ratio of the specific heat of the gas under constant pressure to that under constant volume. The presence of γ in this equation may be explained by the help of the four fundamental thermodynamic relationships. Equation 48 is a special form of the more general expression applicable to the velocity of sound in any medium:

$$V = \sqrt{\frac{\epsilon}{\rho}} \tag{49}$$

where ϵ is the coefficient of elasticity. For a small isothermal compression the coefficient of volume elasticity ϵ is shown from Boyle's law to be equal to the pressure P. This follows on writing

$$PV = (P + \Delta P)(V - \Delta V) = PV + V \cdot \Delta P - P \cdot \Delta V \tag{50}$$

so that

$$\frac{\Delta P \cdot V}{\Delta V} = P = \epsilon \tag{51}$$

In the transmission of a sound wave through a medium the frequency is such that, between the passage of a compression and the following rarefaction, the time intervening is not sufficient for the establishment of thermal equilibrium. The compression and rarefaction may be regarded as approximately adiabatic processes. Thus the numerator ϵ under the radical should not be the isothermal coefficient of volume elasticity

$$\epsilon_T = -V\left(\frac{\partial P}{\partial V}\right)_T \tag{52}$$

but the adiabatic coefficient

$$\epsilon_\phi = -V\left(\frac{\partial P}{\partial V}\right)_\phi \tag{53}$$

It is now to be shown that for gases the ratio of these two quantities leads to the ratio of the specific heats γ $\left(\text{i.e., } \frac{e_\phi}{e_T} = \frac{C_P}{C_V}\right)$. Employing equations 32, 33, 34, and 35, it follows by substitution that

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[11] P. S. Laplace, *Ann. chim.*, **3**, 238 (1816).

$$\frac{\epsilon_\phi}{\epsilon_T} = \frac{-V\left(\frac{\partial P}{\partial V}\right)_\phi}{-V\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\left(\frac{\partial P}{\partial T}\right)_\phi\left(\frac{\partial T}{\partial V}\right)_\phi}{\left(\frac{\partial P}{\partial \phi}\right)_T\left(\frac{\partial \phi}{\partial V}\right)_T} = \frac{\left(\frac{\partial \phi}{\partial V}\right)_P\left(-\frac{\partial P}{\partial \phi}\right)_V}{-\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial \phi}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P\left(-\frac{\partial P}{\partial \phi}\right)_V}{-\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial P}{\partial \phi}\right)_V\left(\frac{\partial \phi}{\partial T}\right)_V} = \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{\left(\frac{\partial Q}{\partial T}\right)_V} = \frac{C_P}{C_P} = \gamma \tag{54}$$

Hence,

$$\epsilon_\phi = \gamma\epsilon_T = \gamma P \tag{55}$$

To be sure, this same result involving γ may be shown more directly from the adiabatic relationship $PV^\gamma = C$.

Differentiation gives for the adiabatic coefficient of elasticity,

$$\epsilon_\phi = -V\left(\frac{\partial P}{\partial V}\right)_\phi = \gamma P \tag{56}$$

Since $\partial P/\partial V$ is inherently negative, the minus sign will disappear.

The Degradation of Energy. In the event that the cycle of the working substance is not reversible, as must always be the case, it follows that when a certain amount of energy is transformed into work, an additional quantity is always made unavailable for ever being employed to do work. This may be illustrated as follows: Suppose T_0 is the temperature of the coldest body available. Let an engine take from the source at a high temperature T_1 a quantity of heat Q_1. This energy has an availability $Q_1 \cdot (T_1 - T_0)/T_1$. Now suppose this first engine exhausts a quantity of heat Q_1' into a condenser at an intermediate temperature T_1'. Of this quantity Q_1' only the amount $Q_1' \cdot (T_1' - T_0)/T_1'$ is available. Hence the loss in availability is

$$Q_1\left(1 - \frac{T_0}{T_1}\right) - Q_1'\left(1 - \frac{T_0}{T_1'}\right) = Q_1 - Q_1' + T_0\left(\frac{Q_1'}{T_1'} - \frac{Q_1}{T_1}\right) \tag{57}$$

The quantity $Q_1 - Q_1$ represents the actual amount of work obtained, but the energy rendered unavailable is greater than this. The last quantity in equation 57 evidently becomes zero only when the gain in entropy for the cycle is zero, or, in other words, when the cycle is reversible. Hence, to conserve available energy, any endeavor to make actual processes approach the ideal reversible cycle is as worthy as an attempt to conserve energy itself.

The Joule-Thomson Experiment. The early experiments of Joule upon the free expansion of gases, as mentioned, page 227, indicated the conclusion that the internal energy was a function of the temperature alone. Professor W. Thomson (later Lord Kelvin) suggested that the small mass of gas used in the expansion should not be expected to produce a measurable change in the temperature of the large amount of water used as the bath. He went to Manchester and cooperated with Joule in carrying out the now famous "porous plug" experiments. In these experiments the gas studied was allowed to pass continuously through an expansion nozzle from a region of high pressure to one of lower value. The expansion nozzle consisted of a plug of either cotton wool or unspun silk, held in place by a boxwood tube. This loose material prevented the formation of violent eddies and the accompanying differences in temperature. The inlet and outlet tubes were well insulated thermally, and in the steady state the pressures and the temperatures on either side of the nozzle were observed. The schematic arrangement of the apparatus is shown in Fig. 113. In their first published report[12] on air, it was stated that on expanding from a pressure P_1 of 34.4 lb. per in.^{2} and a temperature of 15° C., to a pressure P_2 of one atmosphere, the temperature fell 0.3° C.

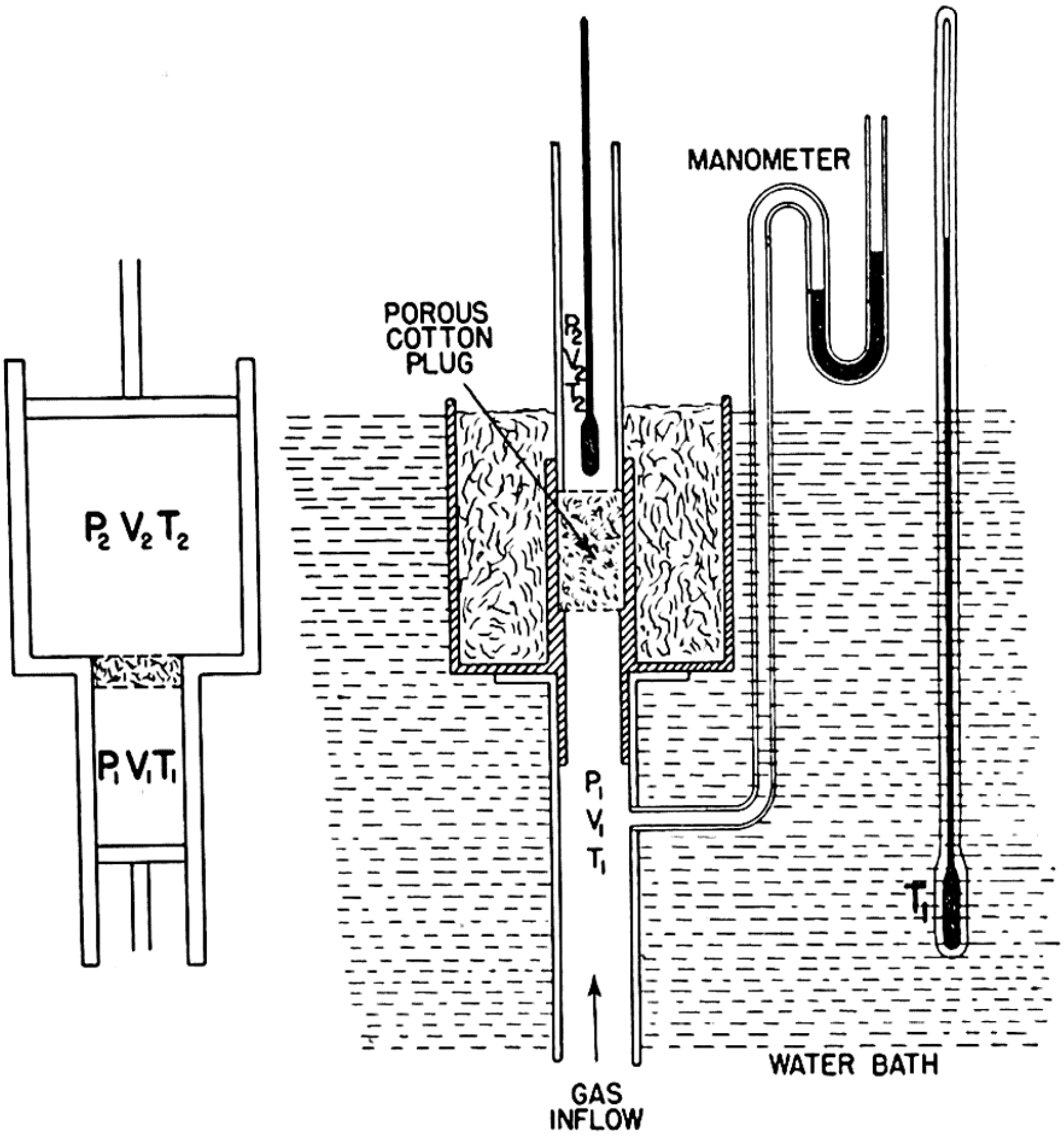

FIG. 113. Schematic arrangement to show expansion in the Joule-Thomson porous plug experiment.

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[12] J. P. Joule and W. Thomson, *Phil. Mag.*, **4**, 481 (1852); **6**, 230 (1853).

Many more exact experiments of this character have since been carried out. Among these may be mentioned the work of Hoxton[13] and that of Roebuck.[14]

Theory of Porous Plug Experiment. The quantity $(U + PV)$ called by Maxwell the " total heat " or the " enthalpy " of the substance, remains constant during the expansion, i.e., by thermal insulation no transfer of heat into or away from the expanding substance is allowed. Now from equation 28

$$\begin{aligned} d(U + PV) &= dQ + V \cdot dP \\ &= \left(\frac{\partial Q}{\partial T}\right)_P dT + \left(\frac{\partial Q}{\partial P}\right)_T dP + V \cdot dP \end{aligned} \tag{58}$$

For an isothermal change, the term in dT vanishes so that

$$\left(\frac{\partial(U + PV)}{\partial P}\right)_T = T\left(\frac{\partial \phi}{\partial P}\right)_T + V \tag{59}$$

For constant enthalpy the right-hand member of equation 58 is zero. On dividing by dP for this condition and combining with equation 59 it follows that

$$T\left(\frac{\partial \phi}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_{U+PV} = -\left[T\left(\frac{\partial \phi}{\partial P}\right)_T + V\right] = -\left[\frac{\partial(U + PV)}{\partial P}\right]_T \tag{60}$$

This may be rewritten as:

$$C_p\left(\frac{\partial T}{\partial P}\right)_{U+PV} = -\left(\frac{\partial U}{\partial P}\right)_T - \left[\frac{\partial(PV)}{\partial P}\right]_T \tag{61}$$

The expression $\partial T/\partial P$ (i.e., the change in temperature per unit change in pressure during expansion) is the experimentally observed quantity in the porous plug experiment. Positive values of this mean a cooling effect upon expansion. The quantity $\partial U/\partial P$ represents the change in internal energy with a change in pressure. Owing to the effect of one particle upon every other, $\partial U/\partial P$ must generally[15] be

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[13] L. G. Hoxton, *Phys. Rev.*, **13**, 438 (1919).

[14] J. R. Roebuck, *Proc. Am. Acad.*, **60**, 537 (1925); J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **48**, 450 (1935).

[15] Exceptions arise for substances whose coefficient of thermal expansion is negative in sign, since

$$\left(\frac{\partial U}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T + T\left(\frac{\partial \phi}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_P$$

The quantity $\left(\frac{\partial V}{\partial P}\right)_T$ is always negative and $\frac{\partial V}{\partial T}$ has the sign of the coefficient of expansion of the substance.

negative in sign because the energy of the system is greatest at the largest volume or the smallest pressure. This then will contribute a cooling effect upon expansion. The term $\partial(PV)/\partial P$ represents the amount by which the gas deviates from Boyle's law. At high temperatures and pressures for all gases it is positive in value (Fig. 102) and hence will contribute a warming effect upon throttling. At ordinary temperatures and not too high pressures most gases behave in the opposite manner so that this effect gives also a cooling upon expansion. This process is utilized in the cumulative cooling of gases in liquefaction by the Linde method. Hydrogen behaves at ordinary temperatures as other gases do at greatly increased temperatures and hence will grow warmer if run through an ordinary air liquefier. However, on sufficient pre-cooling it will liquefy as do other gases.

Inversion Temperature. It must follow that at a certain temperature and pressure neither a heating nor a cooling effect is observed. At this temperature, called the inversion temperature, for a particular pressure

$$\frac{\partial U}{\partial P} = -\frac{\partial(PV)}{\partial P} \tag{62}$$

If $\partial U/\partial P$ be regarded as very small in its contribution to $\partial T/\partial P$, then the inversion points may be regarded as the minimum values of the curves in Fig. 102. This is approximately true for hydrogen.

Equation 60 gives at the inversion temperature:

$$\left(\frac{\partial Q}{\partial P}\right)_T + V = 0 \tag{63}$$

This, by the thermodynamic relationship of equation 35, may be written:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} \tag{64}$$

For a gas that obeys the relationship of van der Waals, equation 64 may be evaluated as

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^2}(V - b)} = \frac{V}{T_i} \tag{65}$$

where T_i represents the temperature of inversion.

Now either P or V may be eliminated by the use of the original equation of van der Waals. On eliminating P it follows that

$$T_i = \frac{2a}{Rb}\left(\frac{V - b}{V}\right) \tag{66}$$

Other Developments of the Clapeyron Equation. *First Method.* Equation 34, so important in processes involving change in state, may be deduced in many alternative ways. Perhaps the simplest method is the following, based upon the expression for the efficiency of a reversible cycle working between two temperatures. If in Fig. 114 the reversible cycle be taken as $ABCD$ between two temperatures very close together as T and $T + dT$ then the heat absorbed (Q_1) is approximately the latent heat of the substance. The work done is the enclosed area, which may be regarded as a rectangle, and is the base ($V_V - V_L$) times the altitude.

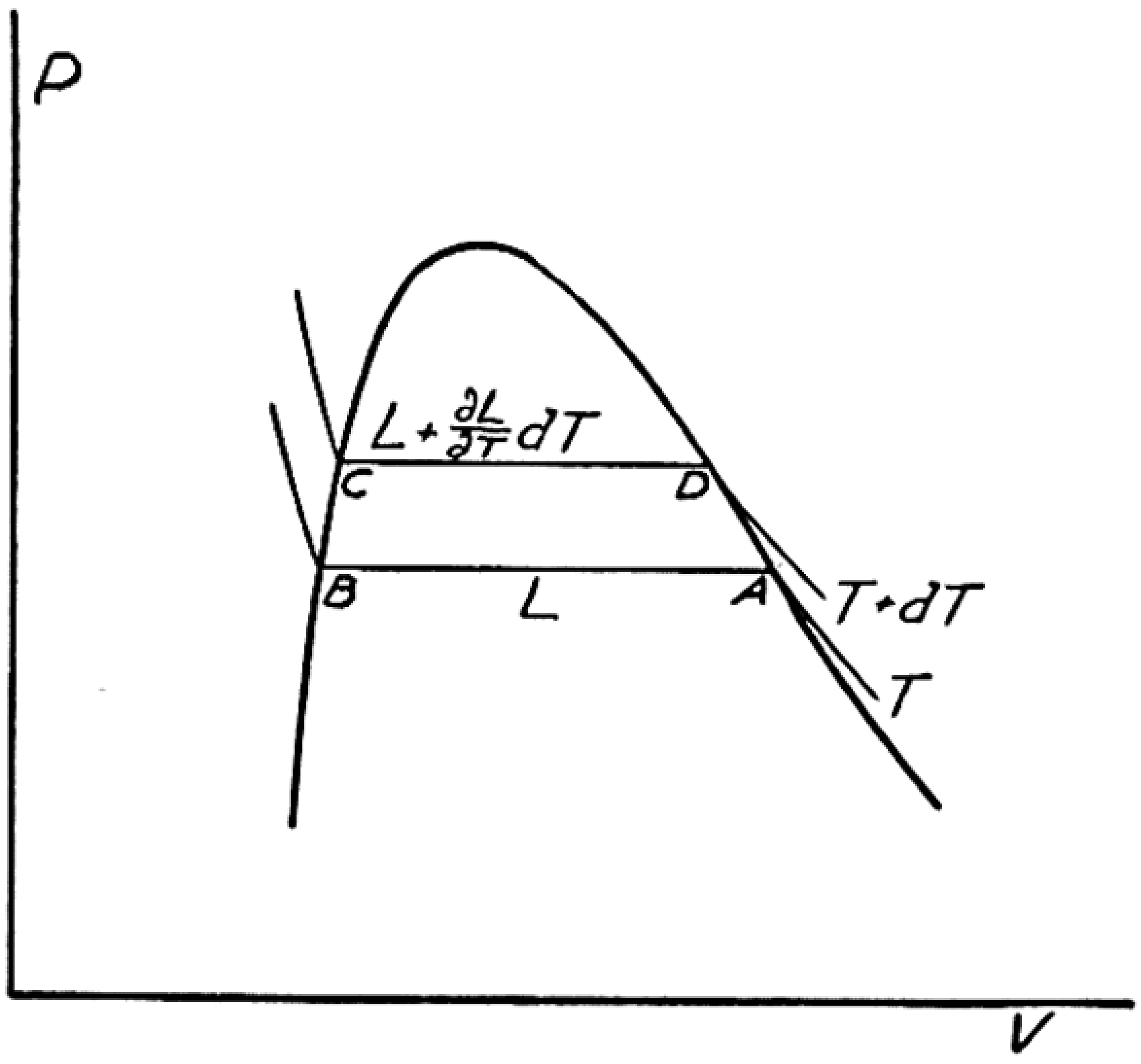

FIG. 114. Reversible cycle involving a liquid and its saturated vapor.

$$\text{Work output} = (V_V - V_L)\left(\frac{\partial P}{\partial T}\right) \cdot dT \tag{67}$$

The output work may also be regarded as equal to the energy input L times the efficiency dT/T. Hence:

$$(V_V - V_L)\left(\frac{\partial P}{\partial T}\right) dT = L \cdot \frac{dT}{T} \tag{68}$$

from which

$$L = T \cdot \frac{\partial P}{\partial T} \cdot (V_V - V_L) \tag{69}$$

Second Method. Another more exact derivation of this expression is as follows: Let it be imagined that unit mass of a substance is taken about the reversible cycle $ABCD$ in Fig. 114 starting at B. Then,

$$C_L\,dT + L_T + \frac{\partial L}{\partial T}\cdot dT - L_T - C_V\,dT = \frac{\partial P}{\partial T}\cdot dT\cdot(V_V - V_L) \quad (70)$$

In this expression, C_L is the specific heat of the liquid, C_V is the specific heat of the saturated vapor, L_T is the latent heat of vaporization at the temperature T, and $\partial L/\partial T$ is the rate of variation of the latent heat with temperature. Then on dividing by dT,

$$C_L - C_V + \frac{\partial L}{\partial T} = \frac{\partial P}{\partial T}(V_V - V_L) \quad (71)$$

For the reversible cycle the change in entropy is zero (i.e., $\Sigma dQ/T = 0$). By using average temperatures this is

$$\frac{C_L\,dT}{T + \frac{dT}{2}} + \frac{L_T + \frac{\partial L}{\partial T}\cdot dT}{T + dT} - \frac{C_V\,dT}{T + \frac{dT}{2}} - \frac{L_T}{T} = 0 \quad (72)$$

Clearing fractions and neglecting powers of dT that are higher than the first gives

$$\frac{L_T}{T} = C_L - C_V + \frac{\partial L}{\partial T} \quad (73)$$

By substitution from equation 71 it follows that

$$L_T = T\cdot\frac{\partial P}{\partial T}(V_V - V_L) \quad (74)$$

which is the desired expression.

The Specific Heat of Saturated Vapors. The justification for the previous development of the Clapeyron equation lies in the information it yields regarding specific heats. In traversing the cycle from B to C the specific heat (C_L) encountered is not that for constant pressure or for constant volume. Instead it is the quantity of heat needed to raise the temperature of a gram of the liquid one degree under such a condition that, if the pressure were maintained constant, the addition of any heat whatever would produce vaporization. For liquids this quantity is approximately the specific heat under constant volume.

From D to A is encountered the specific heat of the saturated gas, C_V. This specific heat under the condition of saturation is quite unlike the specific heats under the condition of constant volume and constant pressure. Strangely enough this quantity may be negative in sign. That is, we may add heat to a saturated vapor and find it after this addition of heat still saturated and at a lower temperature than in the beginning. This possibility is demonstrated by equation 73 which when rewritten has the form

$$C_V = C_L + \frac{\partial L}{\partial T} - \frac{L_T}{T} \tag{75}$$

Illustrating for steam, where T_c denotes the centigrade temperature, the following empirical relationships have been found. The specific heat of water is given perhaps most accurately by Day,[16] whose calculations were based upon the data Rowland obtained in the experiment on the mechanical equivalent of heat. It is sufficient here to use the less exact but simpler expression proposed by Regnault[17] for temperatures above 40° C.:

$$C_L = 1 + 0.00004T_c + \cdots \tag{76}$$

The dependence of the heat of vaporization of water upon the temperature has been expressed by Griffiths[18] and by Henning as

$$L_T = 596.7 - 0.601T_c + \cdots \tag{77}$$

whence it follows that

$$\frac{\partial L}{\partial T} = -0.601 + \cdots \tag{78}$$

and

$$C_V = C_L + \frac{\partial L}{\partial T} - \frac{L_T}{T} = 0.399 - \frac{596.7 - 0.601T_c}{273 + T_c} + \cdots \tag{79}$$

Thus at moderate temperatures a negative value is obtained for C_V, and at a certain high temperature, about 487° C., an inversion occurs, so that above this a positive value exists.

The behavior of a compressed saturated vapor when suddenly allowed to expand indicates the nature of C_V. If such an expansion is accompanied by the formation of a cloud then the specific heat under the condition of saturation is negative. This is illustrated in Fig. 115. Starting with the substance at A, an increase in volume may be accompanied by a change in pressure such that the behavior of the substance is represented by the path *AB*. Then there exists at *B* a mixture of vapor and liquid. To get again a saturated vapor, heat may be added to bring the vapor to the saturated state *C*. Heat has been then added

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[16] W. S. Day, *Phil. Mag.*, **46**, 1 (1898); see also, C. E. Guillaume, *Compt. rend.*, **154**, 1483 (1912).

[17] H. V. Regnault, *Ann. Chim.*, **73**, 5 (1840); see also H. L. Callendar, *Roy. Soc. Phil. Trans.*, **212**, 1 (1912).

[18] E. H. Griffiths, *Phil. Trans.*, **186**, 261 (1896); F. H. Henning, *Ann. Phys.*, **21**, 5, 849 (1906).

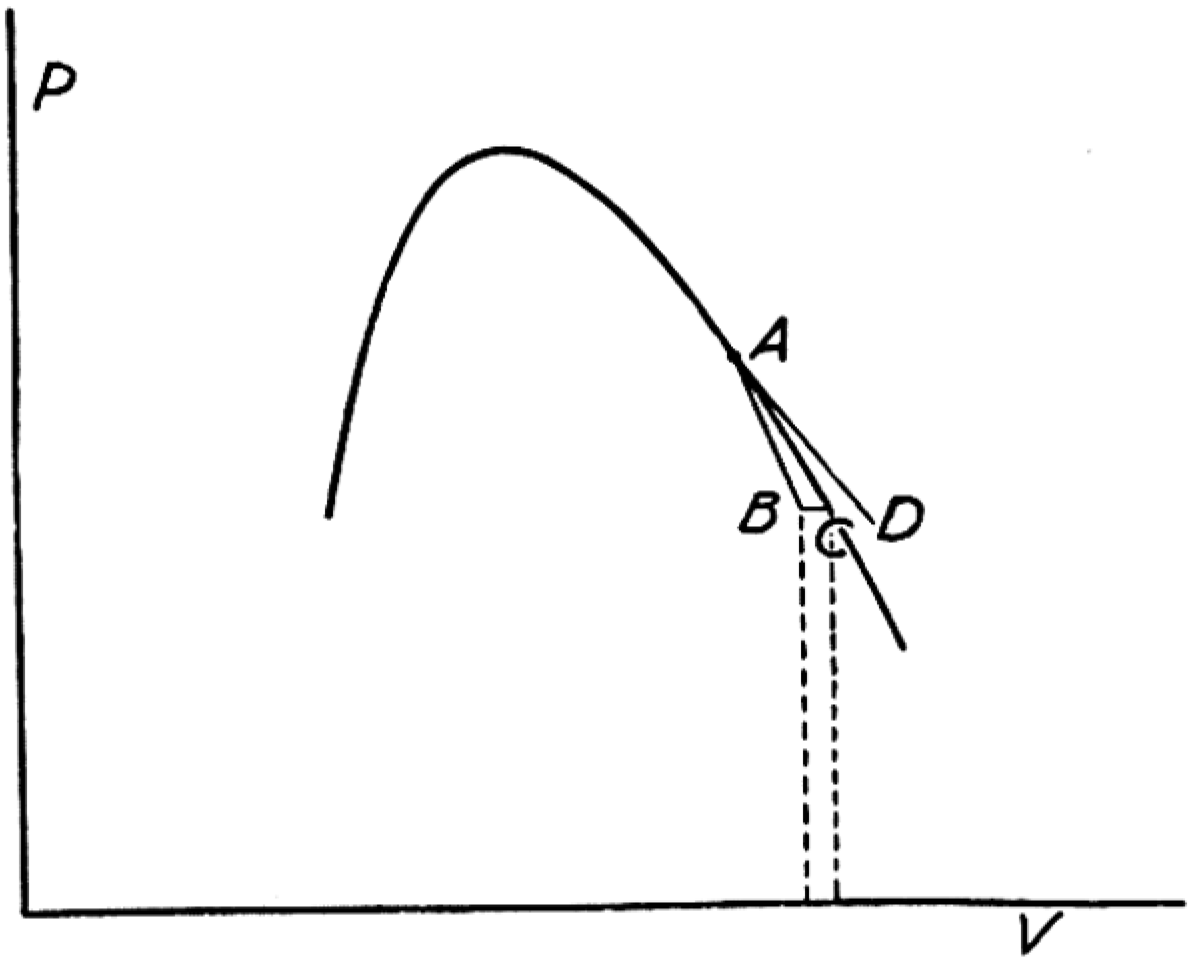

FIG. 115. Figure illustrating the possible behavior of a saturated vapor on expansion.

equivalent to the area under *BC*, yet the final temperature is less than the initial. *AD* represents the path of a vapor with a positive specific heat.

The specific heat of the saturated vapor is of considerable importance in the practical performance of steam engines. The expanding steam in modern turbines although superheated in the beginning soon reaches saturation, and then further expansion results in the formation of droplets. These droplets carried along by the current of steam rapidly wear away the vanes of the final stages of the turbine.

The action of the Wilson cloud chamber in making visible the tracks of ionized particles such as α or β rays is dependent upon the negative specific heat of saturation of the vapor in the chamber. Many of the alcohols, in addition to water, have been found to be satisfactory for this use. The chamber filled with the saturated vapor is subjected to a sudden increase in volume by a lowering of the floor. The ions formed by energetic particle serve as nuclei for the condensing vapor so that a line of cloud droplets delineates the path of the energetic particle.

Difference of Specific Heats for Solids. The difference between the specific heat under constant pressure C_P and that under constant volume C_V may be expressed as follows:

$$C_P - C_V = \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \qquad (80)$$

By considering U as a function of V and T, dU may be written

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{81}$$

and for constant pressure

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{82}$$

By the substitution of equation 82 in equation 80 it follows that

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \tag{83}$$

But from equation 26 $(\partial U/\partial V)_T$ is equal to $T(\partial \phi/\partial V)_T - P$, hence,

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[T\left(\frac{\partial \phi}{\partial V}\right)_T\right] \tag{84}$$

By the third fundamental thermodynamic relationship (equation 34)

$$\left(\frac{\partial \phi}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{85}$$

Since P is a function of T and V, then for a constant pressure

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0 \tag{86}$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial \phi}{\partial V}\right)_T \tag{87}$$

On substitution in equation 84 this gives

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \tag{88}$$

Now $(1/V)(\partial V/\partial T)_P$ is the coefficient of volumetric expansion or 3α where α is the coefficient of linear expansion. The quantity $-V\,\partial P/\partial V$ is the coefficient of volume elasticity ϵ of the substance and is positive since $(\partial P/\partial V)_P$ is inherently negative.

Hence the difference in specific heats may be expressed in terms of the following measurable quantities:

$$C_P - C_V = \frac{9\alpha^2 \epsilon V T}{J} \tag{89}$$

T is the absolute temperature and V is the volume occupied by a gram or a gram-mole of the substance, depending upon whether C_P is the specific heat per gram or per gram-mole. J is the mechanical equivalent of heat. Illustrating for silver:

$$\begin{aligned} \alpha &= 18 \times 10^{-6} \text{ (deg. C.)}^{-1} \\ \epsilon &= 10 \times 10^{11} \text{ dynes per cm.}^2 \\ J &= 4.186 \times 10^{7} \text{ ergs per cal.} \\ V &= 10.28 \text{ cm.}^3 \text{ per gm-atom} \\ \text{at } T &= 373^\circ \text{ K.} \end{aligned}$$

Calculation from equation 89 yields:

$$C_P - C_V = 0.266 \tag{90}$$

The experimental value of C_P for silver is 6.20 cal. per gm-atom. This then gives a value for C_V of 5.93, which agrees well with the classically expected value 5.96.

Nernst Heat Theorem. In 1906, Nernst[19] proposed a general principle which he called "the new heat theorem." This principle is often referred to as the third law of thermodynamics. In this the energy content of a system is represented by the negative value of some function U, dependent upon the volume and the temperature, such that, if the system change, $U_2 - U_1$ is independent of the route by which the initial and final states are connected. Another quantity A similarly applicable to isothermal transformations is introduced, such that $A_2 - A_1$ represents the maximum external work that can be obtained in the change considered. The concepts U and A are analogous to total energy and free energy respectively.

Certain deductions particularly important at low temperatures have been shown to follow. Among these are that as T approaches the absolute zero

$$\frac{dA}{dT} = 0 \tag{91}$$

that is to say, close to the absolute zero the maximum work which can be gained is independent of the temperature.

In a similar way it follows as shown by Planck that

$$\lim_{T \to 0} \frac{dU}{dT} = 0 \tag{92}$$

This result has been interpreted by some as indicating a limiting low value of the specific heat at absolute zero, whereas others would conclude that the atomic heat itself becomes zero.

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[19] W. Nernst, *Nach. Ges. Wiss. Göttingen*, Jan., 1906; *The New Heat Theorem*, E. P. Dutton and Company, 1926.

Other consequences are that

$$\lim_{T \to 0} \frac{dP}{dT} = 0 \tag{93}$$

and

$$\lim_{T \to 0} \frac{dV}{dT} = 0 \tag{94}$$

i.e., both the thermal coefficient of pressure of a gas and the coefficient of volume expansion like the specific heat disappear at absolute zero. This result is in agreement with the observation of Grüneisen regarding specific heats and linear coefficients of expansion.

QUESTIONS AND PROBLEMS

1. Show that a reversible engine working between any two temperatures has the maximum efficiency of any cycle operating between those temperatures.
2. The vapor tension of water at 99.5° C. is 746.48 mm. and at 100.5° C. it is 773.73 mm. of mercury. The specific volume of saturated steam at 100° C. is 1,671 cm.^{3} per gm., and the density of water at the same temperature is 0.9584 gm. per cm.^{3}. Calculate the latent heat of vaporization of water at 100° C.
3. An increase in pressure of 1 atmosphere lowers the freezing point of water 0.0073° at 0° C. The density of ice is 0.9162 gm. per cm.^{3} and of water is 0.99987 gm. per cm.^{3} at 0° C. Calculate the latent heat of fusion of ice at 0° C.
4. Show that the sublimation curve of a substance is not its vapor-tension curve extended beyond the triple point.
5. The low-temperature coils of a mechanical refrigerator are at a temperature of −40° C. and the compressed gas has a temperature of 60° C. Express the maximum efficiency.
6. Using the data of Table 20, calculate the Peltier coefficient for the iron versus constantan couple at 100° C.

CHAPTER IX

THE PRODUCTION OF HIGH AND LOW TEMPERATURES

HIGH TEMPERATURES

The Combustion Furnace and the Electric Furnace. The use of combustion as a source of heat antedates the earliest writings of man. In modern fuel-heated processes a large proportion of the heat that is developed is carried away by the waste flue gases. Further, the heat is usually developed in a chamber which is separated from the material to be heated by refractory walls of low thermal conductivity. These facts necessarily result in a low efficiency for the method of heating by combustion. The average efficiency for such processes is probably less than 15 per cent.

In the electrical method of heating there are no end products to be discharged. Combining with this the possibility of developing the heat directly in the same refractory enclosure with the material to be heated, the operation of the electric furnace may often be carried out with an efficiency of more than 80 per cent.

The highest temperatures obtainable with the combustion furnace are limited by the same factors which limit its efficiency. Under the most favorable circumstances, such as in the surface combustion process in which hydrogen and oxygen are introduced in the exact proportion to form water, temperatures approaching 2,000° C. have been attained. No such limitation is encountered in the electric method.

The above features of the electric furnace, together with the fact that its temperature may be more easily and accurately controlled, often more than offset the apparent cheaper cost of operation of the fuel-heated furnace. This has resulted in the extensive substitution in industrial processes of electrical furnaces for those of other types originally used.

Electric Conduction Furnaces. The use of an electric current to heat the conductor through which it flows was employed as early as 1810. At that time, Davy successfully melted iron wire by passing the current from a voltaic battery through it. This method of heating has now wide application in practice.

The type of resistor elements employed in the furnace is determined by the conditions to be met in any particular application. For temperatures up to 1,200° C. many alloys of iron, nickel, and chromium, with admirable properties, have been developed. Platinum is suitable for temperatures approaching its melting point (1,755° C.). For still higher temperatures, tungsten in a suitable atmosphere (i.e., hydrogen or vacuum) may be used well above 2,000° C., and carbon whose melting point is approximately 3,500° C. is the most refractory conductor available. A tubular carbon furnace with water-cooled electrodes is shown in Fig. 116. When it is placed in a vacuum and made to carry sufficiently large currents, temperatures above 2,500° are readily attained in the hollow cylindrical cavity.

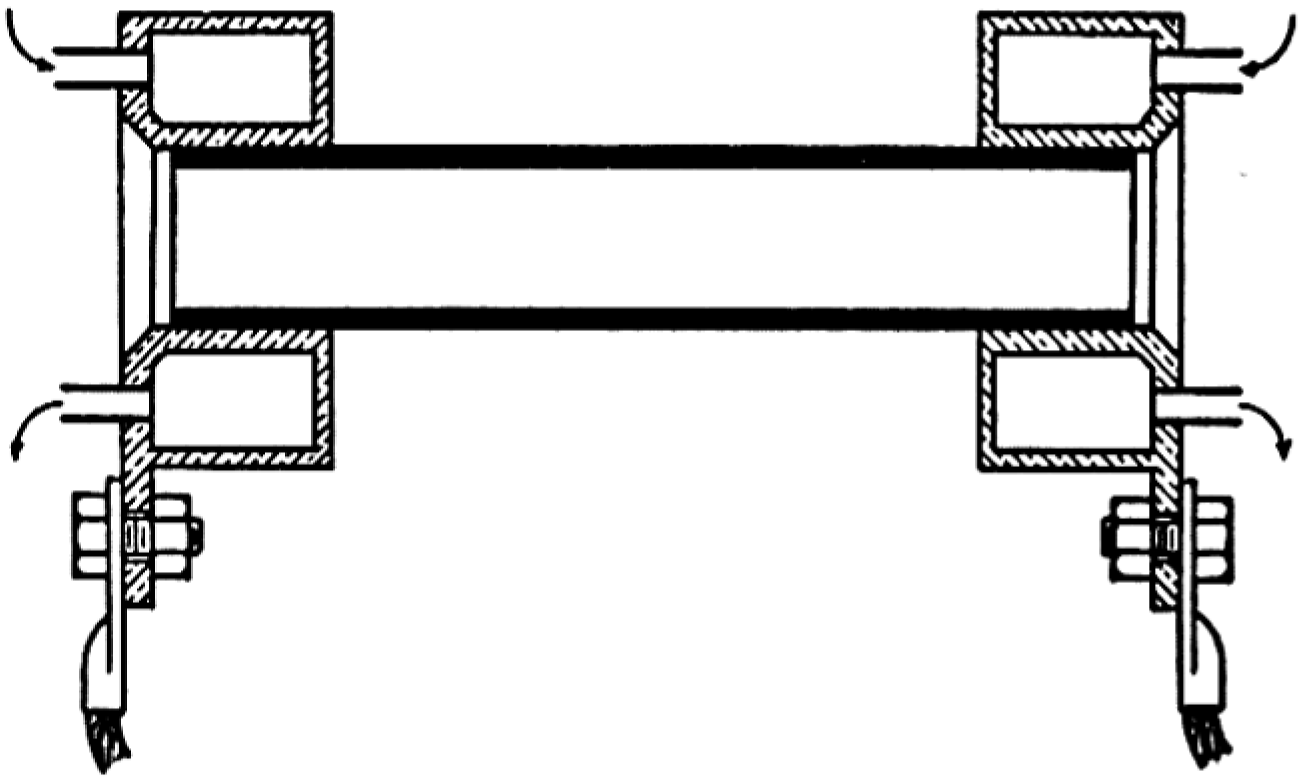

FIG. 116. Hollow carbon-tube furnace for very high temperatures.

Materials often employed as supporting forms for the resistor elements are porcelain, quartz, alundum, or refractory alkaline earth oxides. These must be chosen with proper regard for possible chemical activity with the material being heated.

Electric Arc Furnaces. The electric arc as a heating agent was probably first employed by Berthelot[1] in 1862. In his arrangement the electrodes were two horizontal carbon rods one of which was made hollow to allow any gas desired to be forced through it into the arc. By using a stream of hydrogen into the arc the synthesis of acetylene was demonstrated. Several forms of arc furnaces were designed for practical purposes by Siemens[2] about 1877. In 1887 Heroult designed a successful electrolytic arc furnace for the production of aluminum.

Commencing in 1892, a remarkable series of experiments with the electric arc furnace was carried out by Moissan.[3] The refractory metals such as chromium, molybdenum, and tungsten were melted for the first time. Similarly many hitherto irreducible oxides were transformed by the action of the carbon at the high temperatures to pure metals or to metallic carbides. The type of furnace generally employed by Moissan made use of horizontal electrodes, as shown in Fig. 117. The refractory walls and cover of the enclosure were thick slabs of lime. The highest terrestrial temperatures attained anywhere until very recently were undoubtedly reached by Moissan. By decreasing the size of the cavity in which the energy is dissipated and increasing the electrical power input as well as the thermal insulation of the cavity, there would appear to be no limit to the maximum attainable temperature. In practice, however, the power losses become very great as the temperature increases, so that, under the most favorable experimental conditions Moissan could arrange, a temperature of 3,500° C. could not be exceeded.

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[1] M. Berthelot, *Compt. rend.*, **53**, 640 (1862).

[2] C. W. Siemens, *Nature*, **16** (1877); *Brit. Assoc. Report*, p. 496, 1882.

[3] H. Moissan, *Compt. Rend.*, **115**, 1031, *et seq.* (1892).

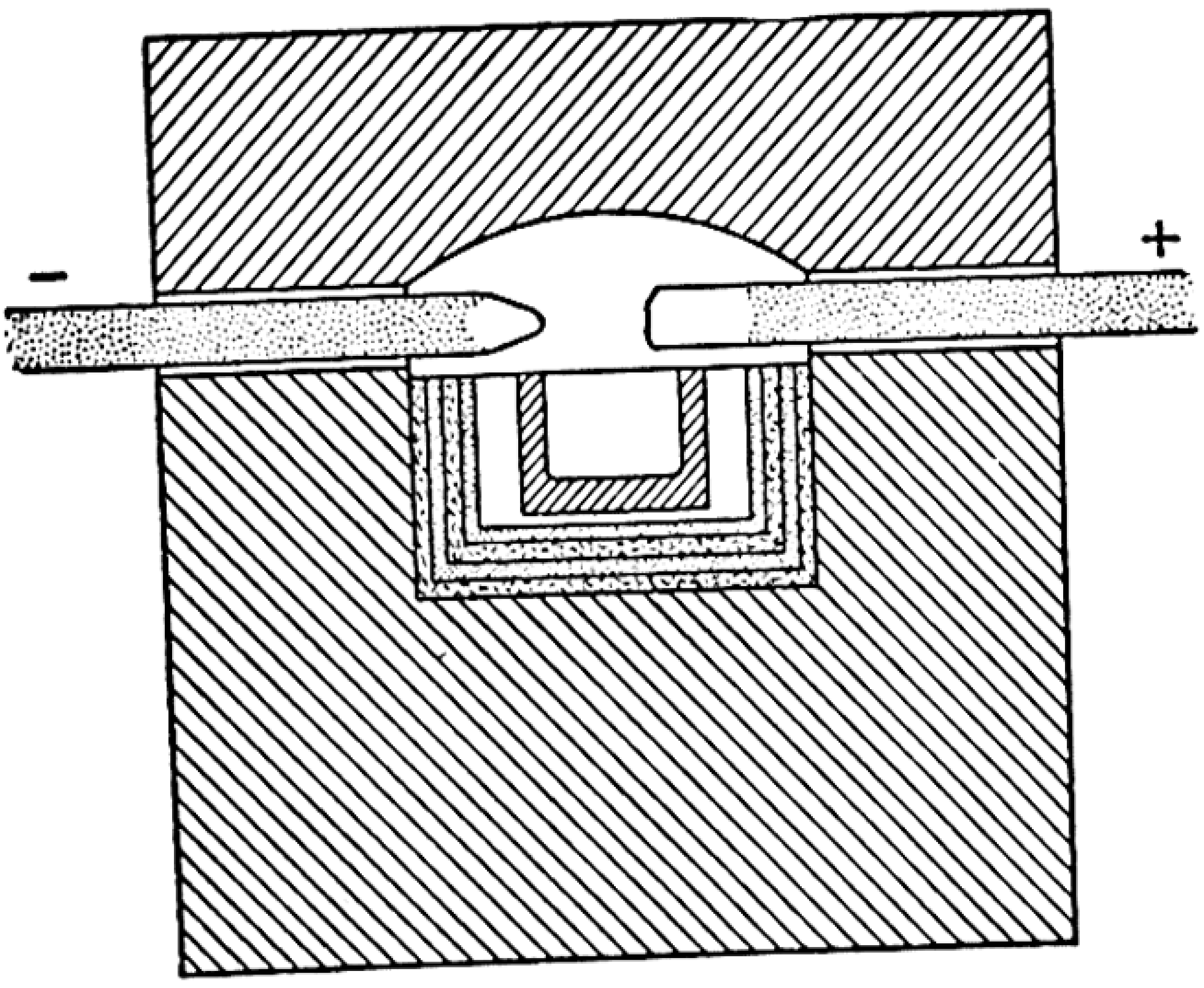

FIG. 117. The arc furnace of Moissan.

The application of the electric arc furnace to industrial processes was given great impetus in 1898 through the development of an arc furnace for the production of iron from the ore, by Stassano in Italy.

In the modern production of steel from iron, the arc furnace is used extensively. Single units for this purpose have been constructed with a capacity as great as 60 tons at one melting. These furnaces generally have many electrodes and operate on polyphase electric circuits.

The Low-Frequency Induction Furnace. Electric induction furnaces operating on a low-frequency circuit, as shown in Fig. 118, have been used extensively in the manufacture of steel and high-melting-point alloys. Furnaces of this type were probably first used by Ferranti in 1887. This furnace is really a step-down electrical transformer. The secondary consists of a ring of the material *M* to be heated which is placed in a trough in a refractory support. The primary coil *P* of many turns gives rise to an alternating magnetic flux in the iron core. This varying magnetic flux threads the single-turn secondary and induces in it a low-valued alternating voltage. Neglecting the magnetization current there will be set up in the secondary of a single turn a current which is as many times that in the primary coil as there are primary turns.

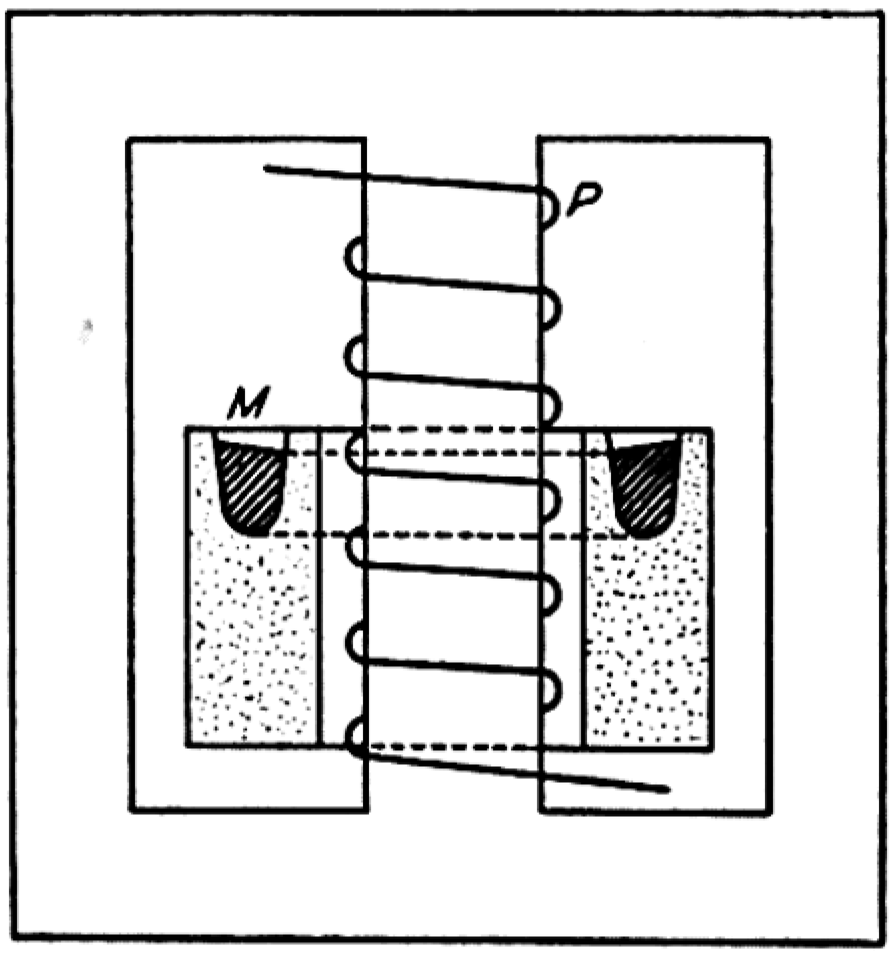

FIG. 118. The low-frequency induction furnace.

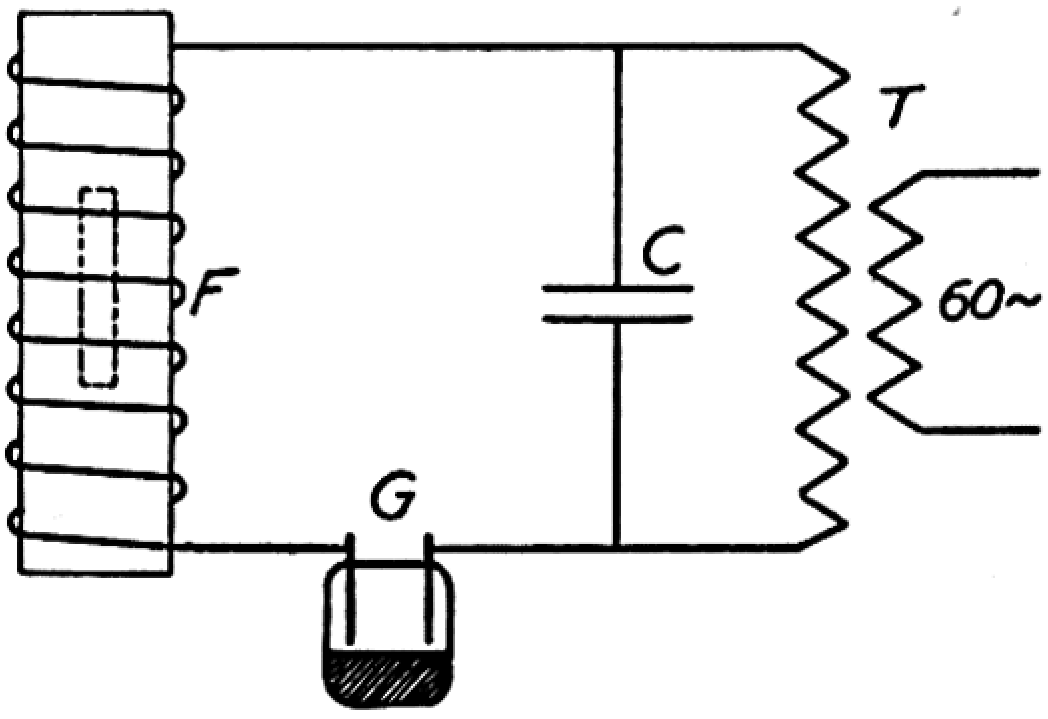

FIG. 119. The high-frequency induction furnace.

The material melted may thus be maintained entirely free from contamination due to contacts with electrodes or foreign gases. From the electromagnetic forces due to the varying current an agitation of the heated material results. This is a desirable factor in the fabrication of alloys.

High-Frequency Induction Furnace. A method of heating by causing high-frequency induced "eddy" currents to be set up in the material has been developed by Northrup.[4] The material to be heated is contained in a crucible and is placed at the center of a cylindrical water-cooled helical coil which constitutes the inductance of an oscillatory circuit. The arrangement of apparatus as used by Northrup is shown in Fig. 119. The high-potential 60-cycle transformer *T* with an output of about 10,000 volts is connected to a condenser of suitable capacity *C*. Across the terminals of the condenser is connected the furnace coil *F* in series with a spark gap *G*. This gap may consist of cold mercury electrodes in an evacuated bulb, or graphite electrodes over mercury in a suitable atmosphere such as hydrogen or alcohol vapor. The characteristics of the gap should be such that its resistance breaks down at almost the peak of the high-potential wave. This breakdown is followed by a number of high-frequency oscillations, after which the resistance of the gap is abruptly re-established. The electrical constants of the circuit are usually such that its natural frequency lies between 10 and 100 kilocycles.

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[4] E. F. Northrup, *Trans. Amer. Elec. Soc.*, **35**, 69 (1919).

Instead of this Tesla oscillatory circuit, a single unit generator of the Alexanderson type may be employed. Such generators have been built with a possible output of 200 kw. at 25 kilocycles. High-capacity vacuum-tube oscillators might be employed equally well. A push-pull circuit of this type is shown in Fig. 120. A direct voltage as great as 15,000 volts may be applied to the anodes. The output coil which constitutes the furnace is connected between the two anodes. This coil consists of a few turns of hollow copper tubing, cooled by flowing water, and determines by its capacity and inductance the frequency of the oscillation.

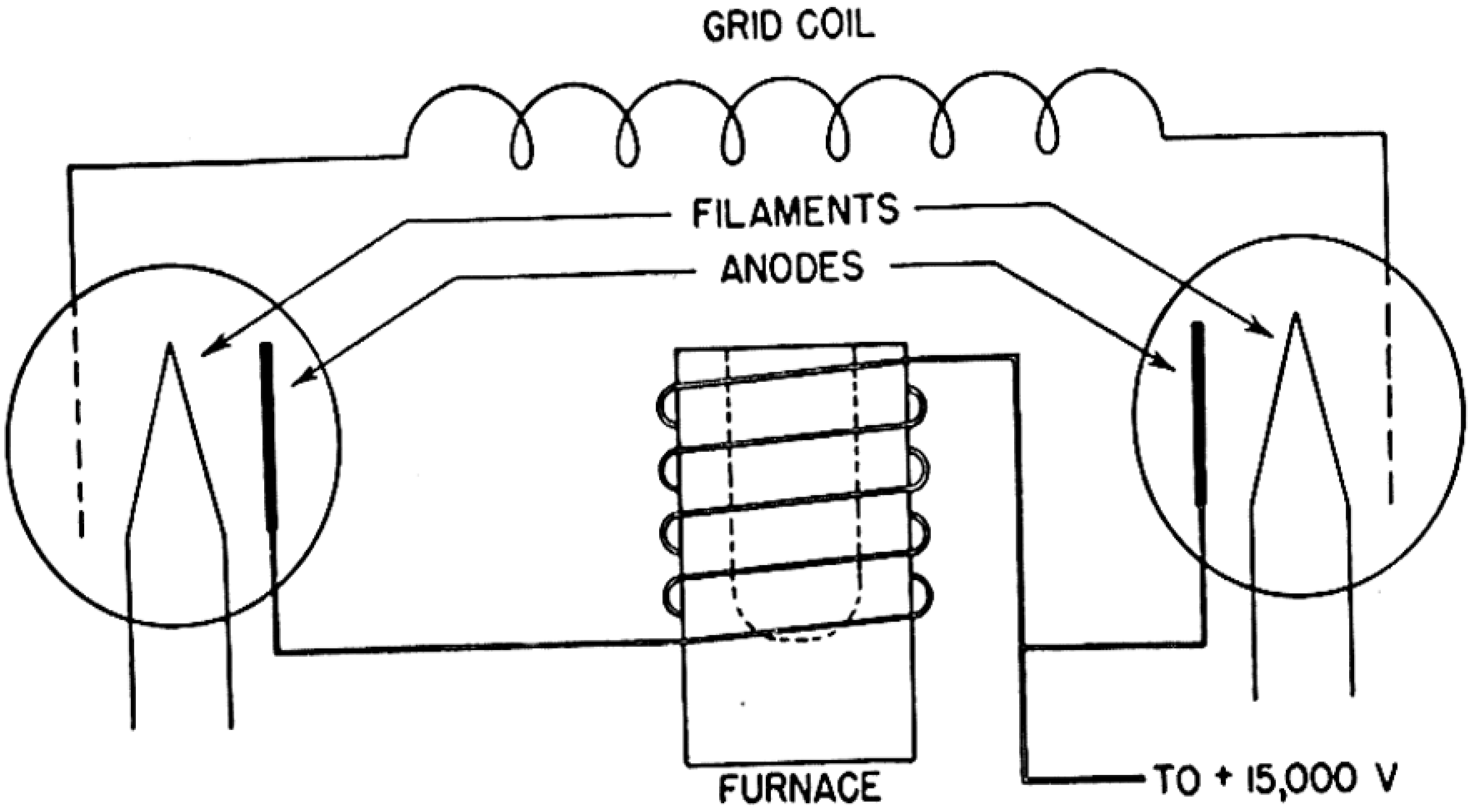

FIG. 120. High-frequency induction furnace, using power oscillator tubes.

Temperatures attainable in such furnaces are limited entirely by the thermal insulation of the material being heated. In recent tests by Dr. Chesnut, a hollow graphite block has been employed as the conductor, in which the high-frequency induced currents were set up. This was surrounded by lampblack for the purpose of thermal insulation. Temperatures above 3,000° C. have been maintained over a long period.

The Exploded Wire by Condenser Discharge. A minute source of heat at an exceedingly high temperature for a momentary duration has been described by Anderson.[5] In this method a condenser C of about 14-microfarad capacity was charged to a potential V of 26,000 volts and discharged instantaneously through a very fine short wire. The duration of the discharge was estimated as 10^{-5} second. Thus the dissipation of this amount of energy ($\frac{1}{2}CV^2$) represented a momentary power application of about 12,600 kw. This energy (30 cal.) stored in the wire, whose mass was only about 2 mg., ideally would have elevated its temperature 150,000° C. Actually, an estimate of the highest temperature attained was reported as 20,000° C. The intrinsic brightness of the source was about one hundred times that of the sun.

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[5] J. A. Anderson, *Astrophys. Jour.*, **51**, 37 (1920).

The Sun as High-Temperature Source. For the development of a source having an extremely high temperature, perhaps the sun's radiation offers the most unlimited opportunity. Many devices to concentrate this radiation and thereby develop high temperatures have been attempted. The distance between the sun and the earth is about 220 times the radius of the sun. Hence any lens or mirror (functioning ideally) whose diameter of reception is 220 times the diameter of the image formed will result in an intensity of radiation at the image comparable with that at the surface of the sun. An imaginary, totally black, thin disk with a reflecting back would then, if placed at this focus, attain the sun's temperature. The total energy per second per square meter normal to the solar radiation amounts to about 1,350 joules. At an efficiency of 100 per cent this is sufficient to operate continuously an engine of power 1.35 kilowatt or 1.8 horsepower.

LOW TEMPERATURES

Freezing Solutions. Many salts when in contact with ice in excess quantities form a saline solution which in turn dissolves more ice. The transformation of this ice into water demands the reception of a definite quantity of heat per unit mass, and if the mixture is thermally insulated the heat will come from the internal energy of the mixture itself. This water formed, in turn dissolves more salt, keeping the concentration always at a definite value. A course of action of this type is illustrated in Fig. 121 for a mixture of ice and ammonium sulphate. Thus if ice and salt are mixed at 0° as shown by point A, then, as ice melts, enough salt will dissolve in the water formed to make a solution of 42 per cent ammonium sulphate by weight. This in turn dissolves more ice, forming a solution of slightly less concentration at a continuously lower temperature if the mixture is thermally insulated. This action continues until the point C is reached, under which condition a minimum temperature has been attained ($-19.1°$ C. at a concentration of 38 per cent). If not thermally insulated, the solution process will continue at a speed determined by the rate at which heat is communicated. The point C might be similarly approached along the curve from B.

For sodium chloride the curve *AC* is slightly more complicated than for ammonium sulphate in that it has a point of discontinuity at *A*.

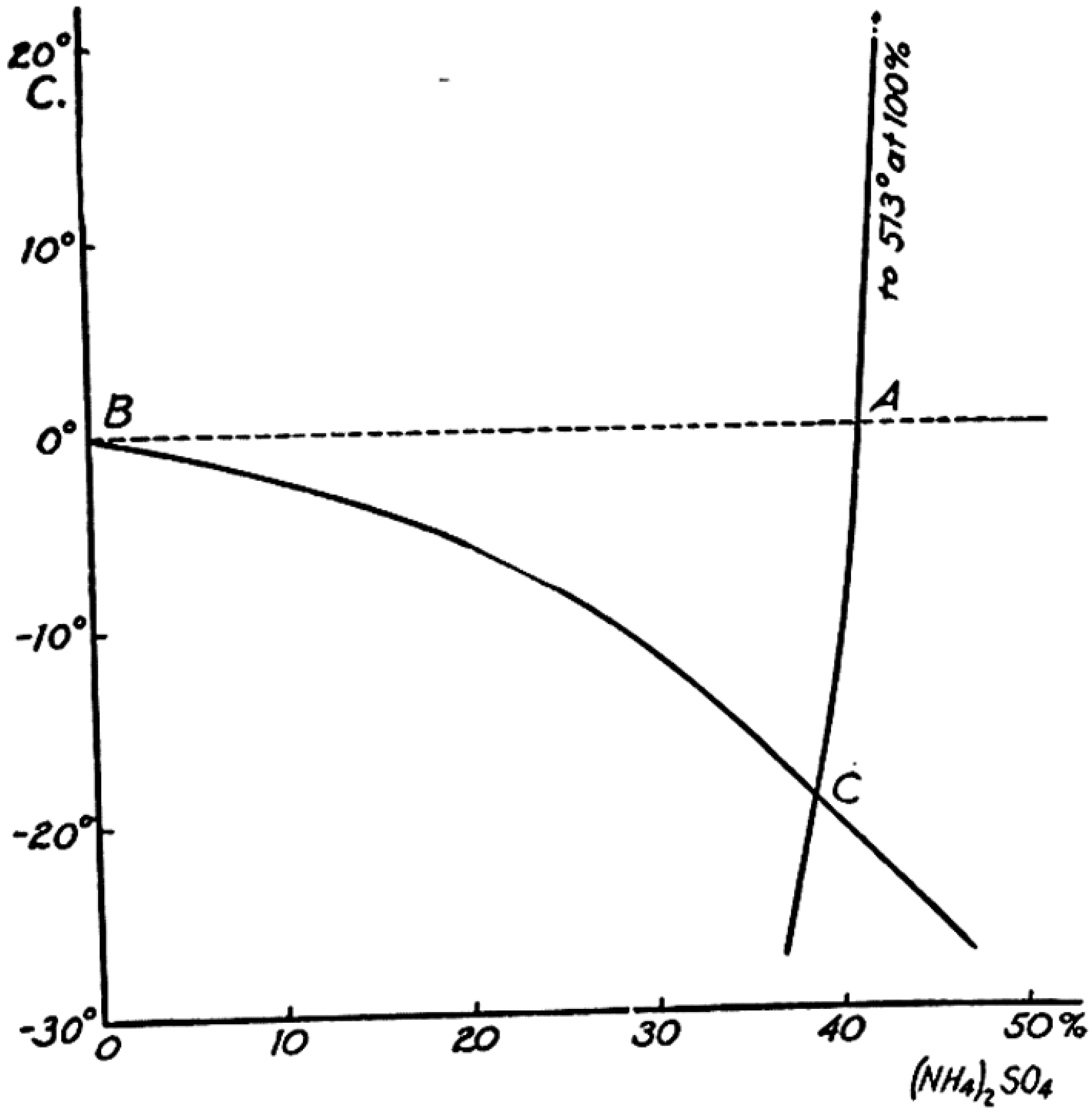

FIG. 121. Equilibrium diagram for ice and ammonium sulphate.

Refrigeration — Mechanical. On page 236, there was discussed the possibility of a working substance being taken about a Carnot cycle in a reverse direction. That is, the working substance absorbs a quantity of heat Q_2 from the source at a low temperature; it then receives an amount of work W and ejects a quantity of heat Q to the reservoir at the high temperature. If accompanying this process there occurs also a continuous change of state, one has the arrangement commonly employed in mechanical refrigerators. A schematic diagram of this arrangement is shown in Fig. 122. The compressor B forces the vapor into a cooling system such that the temperature and pressure transform

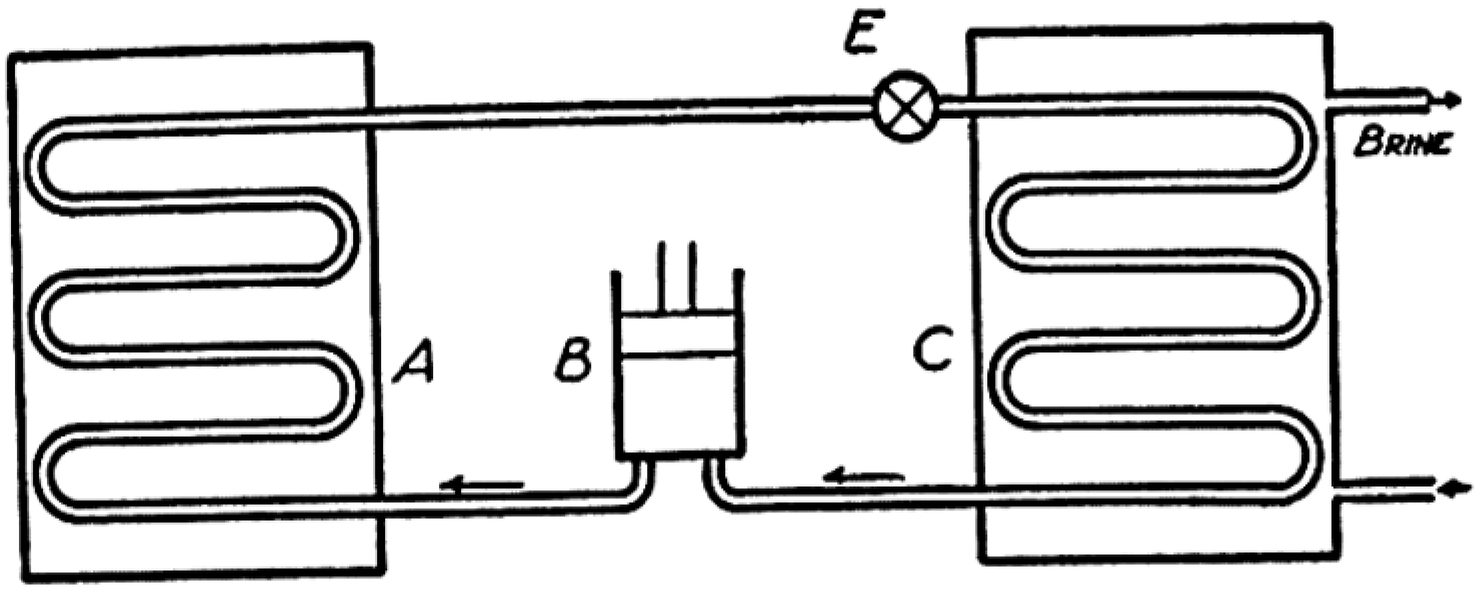

FIG. 122. Mechanical refrigerating system.

the vapor into a liquid. The heat of vaporization is dissipated by the cooling mechanism, which may be a stream of water or air.

The liquid is now allowed to pass the valve *E* into a region of sufficiently reduced pressure for boiling to occur. The heat of vaporization is then absorbed from the surroundings, which may be a circulating brine bath or the space to be cooled.

Some Common Refrigerating Substances. Some materials commonly employed in refrigerators of this type are carbon dioxide (CO_2), ammonia (NH_3), sulphur dioxide (SO_2), and many specially developed organic materials as typified by the compound dichlorodifluoromethane (CCl_2F_2) commonly known as freon. The choice of material employed is dependent upon the conditions to be encountered in practice. The properties of the material to be considered are its latent heat of vaporization, its density, and its vapor pressure at a low temperature.

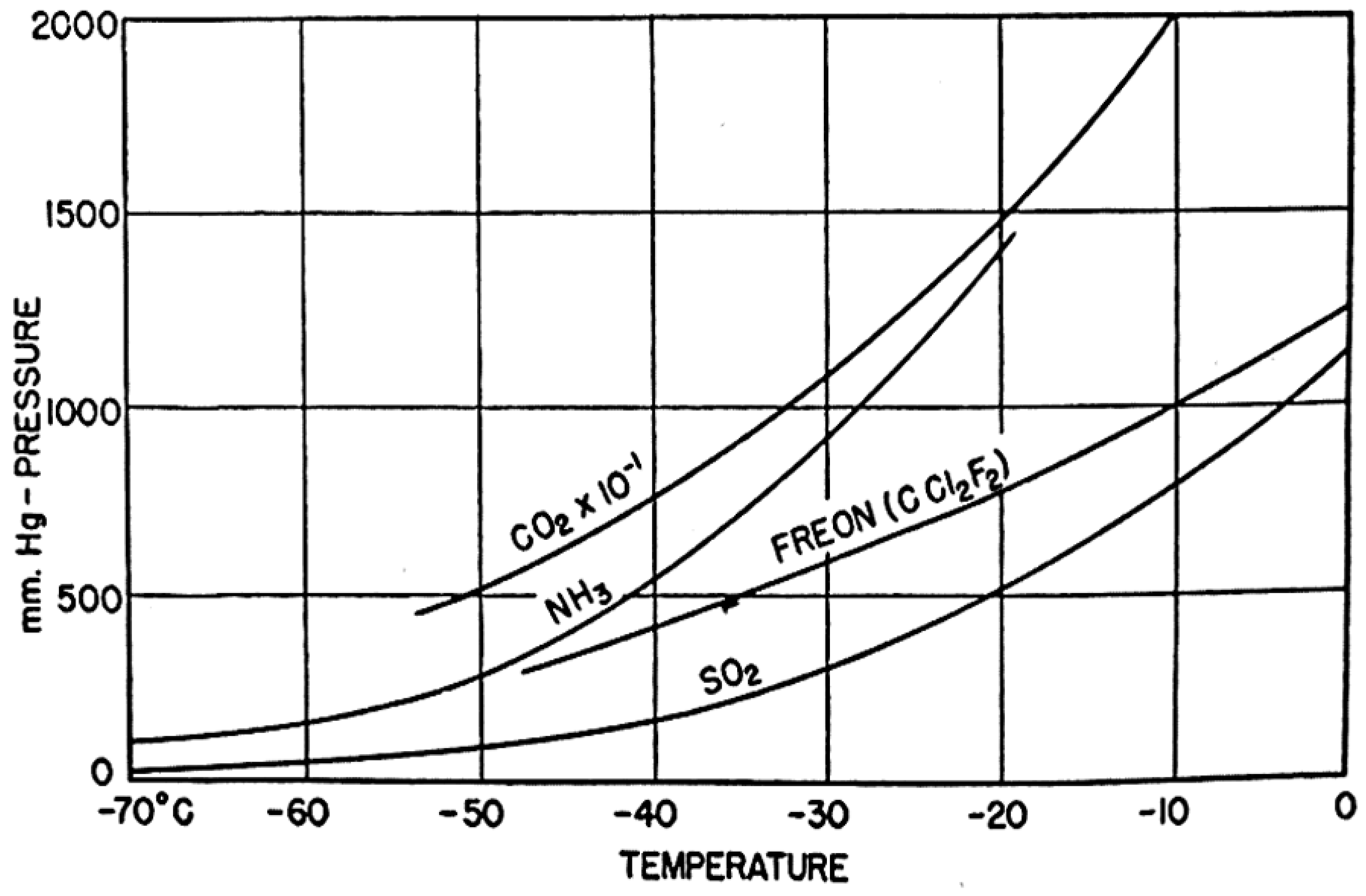

FIG. 123. Vapor-tension curves for various refrigerating materials.

The relative values of the vapor pressures of the substances mentioned are shown in Fig. 123. At −30° C. the vapor pressures in millimeters of mercury are respectively: SO_2, 330 mm.; NH_3, 853 mm.; CO_2 11,630 mm.; and freon, 621.4 mm. The density of the substance is an important factor in determining the dimensions of the apparatus, when the quantity of material to be circulated per unit time is known. The densities of the above-mentioned vapors at their corresponding pressures at a temperature of 30° C. are respectively as follows: SO_2, 0.00128 gm. per cm.^{3}; NH_3, 0.00096 gm. per cm.^{3}; CO_2, 0.0391 gm. per cm.^{3} and freon, 0.00512 gm. per cm.^{3} The values of the latent heats of vaporization for the substances are respectively: SO_2, 100 cal. per gm.; NH_3, 325 cal. per gm.; CO_2, 75 cal. per gm.; and freon 44 cal. per gm.

It is thus evident that in using CO_2 the apparatus may be greatly reduced in size. It is, however, more subject to leaks, because of the very high pressure. Such devices are commonly employed where small space is the primary consideration, such as on shipboard. The tendency for leaks with SO_2 and NH_3 is very small since their vapor pressures are not greatly different from atmospheric pressure.

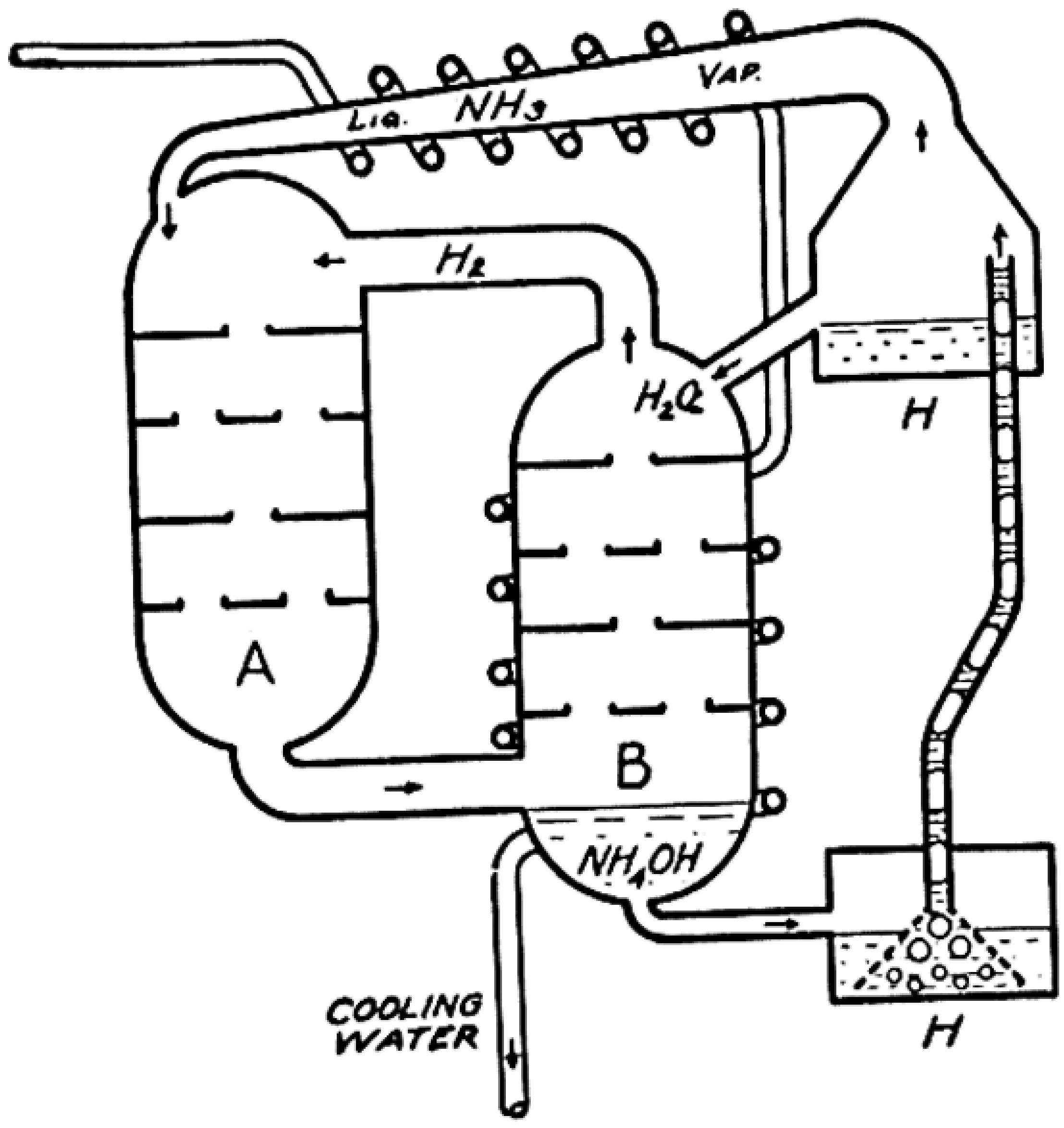

FIG. 124. Refrigeration by the application of heat.

Refrigeration by Combustion. A type of refrigerator employing burning gas to actuate the cooling cycle is shown schematically in Fig. 124. The cooling in this device occurs in chamber *A*, in which liquid ammonia entering at the top vaporizes in a stream of hydrogen also entering from the top. The heat of vaporization is supplied from the surrounding chamber being cooled. The current of hydrogen and ammonia vapor enters chamber *B* at the bottom, and in passing upward encounters a downward stream of water which dissolves the ammonia vapor and carries it along to *C*. From *C*, by percolator action, the ammonium hydroxide is elevated to *D*, where the action of the flame again separates it into ammonia vapor and water. The water again enters chamber *B* at the top, completing the water cycle. The ammonia vapor passing along *E* is cooled by the external circulating stream of water to a temperature such that, under the pressure existing within the system, liquid ammonia is formed.

The evident advantage of this arrangement is complete freedom from all moving parts.

Very Low Temperatures, Pictet or Cascade Method. In 1877, by the arrangement of cycles of the type shown in Fig. 122, Pictet[6] and Cailletet[7] working independently were able to liquefy oxygen. The extension of this method enabled Dewar[8] in 1893 to liquefy air and then hydrogen in 1898. The apparatus in the form employed by Dewar is shown in principle in Fig. 125. The first cycle is that of carbon dioxide, which upon evaporating in chamber *A* cools it to about −79° C. This serves as a cooler for the compressed ethylene of the next cycle, causing it to liquefy. The liquid ethylene evaporates under reduced pressure in chamber *B*, reducing its temperature below the critical temperature of the material of the next stage, oxygen. For the more permanent gases additional stages are added.

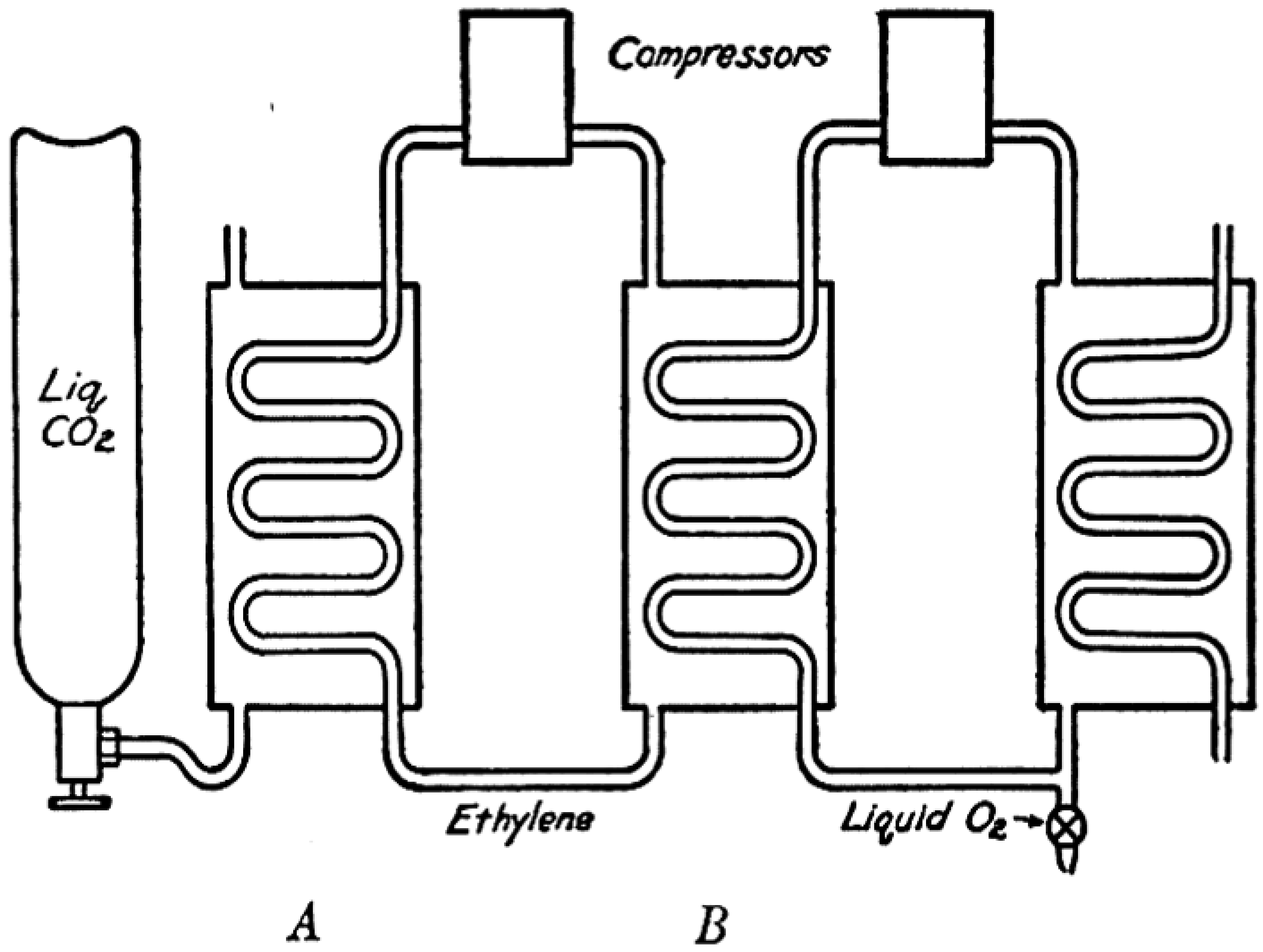

FIG. 125. Liquefaction of gases by the cascade or Pictet process.

The Regenerative or Linde Method. The cooling effect produced by most gases when they are allowed to expand through a jet to a region of reduced pressure serves as a possible method of producing low temperatures. The suggestion of this possibility is attributed to various investigators, but it was first successfully applied by Linde[9] in 1896. A modification of this apparatus was used almost at the same time by Hampson.[10] The apparatus as usually employed is shown diagrammatically in Fig. 126. The method as used for air is as follows: Air at a pressure of 1 atmosphere with all water vapor and carbon dioxide removed is compressed by C_1 to a pressure of about 16 atmospheres. The compressor C_2, besides receiving the output of C_1, receives a certain amount of air rejected by the liquefier at the same pressure, and compresses the whole to about 200 atmospheres. The output of C_2, hot because of a partially adiabatic compression, is cooled by an ice bath and thence conducted to the liquefier. Here it expands through the nozzle N_1 to a pressure of 16 atmospheres. After this expansion about four-fifths of the gas travels back along the outside of the inlet pipe so as to cool

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[6] R. Pictet, *Compt. rend., Acad. Sci. Paris*, **86**, 37 (1878).

[7] L. Cailletet, *Compt. rend., Acad. Sci. Paris*, **86**, 97 (1878); **85**, 1270 (1877).

[8] Sir James Dewar, *Proc. Roy. Inst.*, **14**, 1 (1896); *Roy. Soc. Proc.*, **63**, 256 (1898).

[9] C. Linde, *Ann. phys. chem.*, **57**, 328 (1896); *Génie civil*, **31**, 35 (1897).

[10] W. Hampson, *Nature*, **55**, 485 (1897).

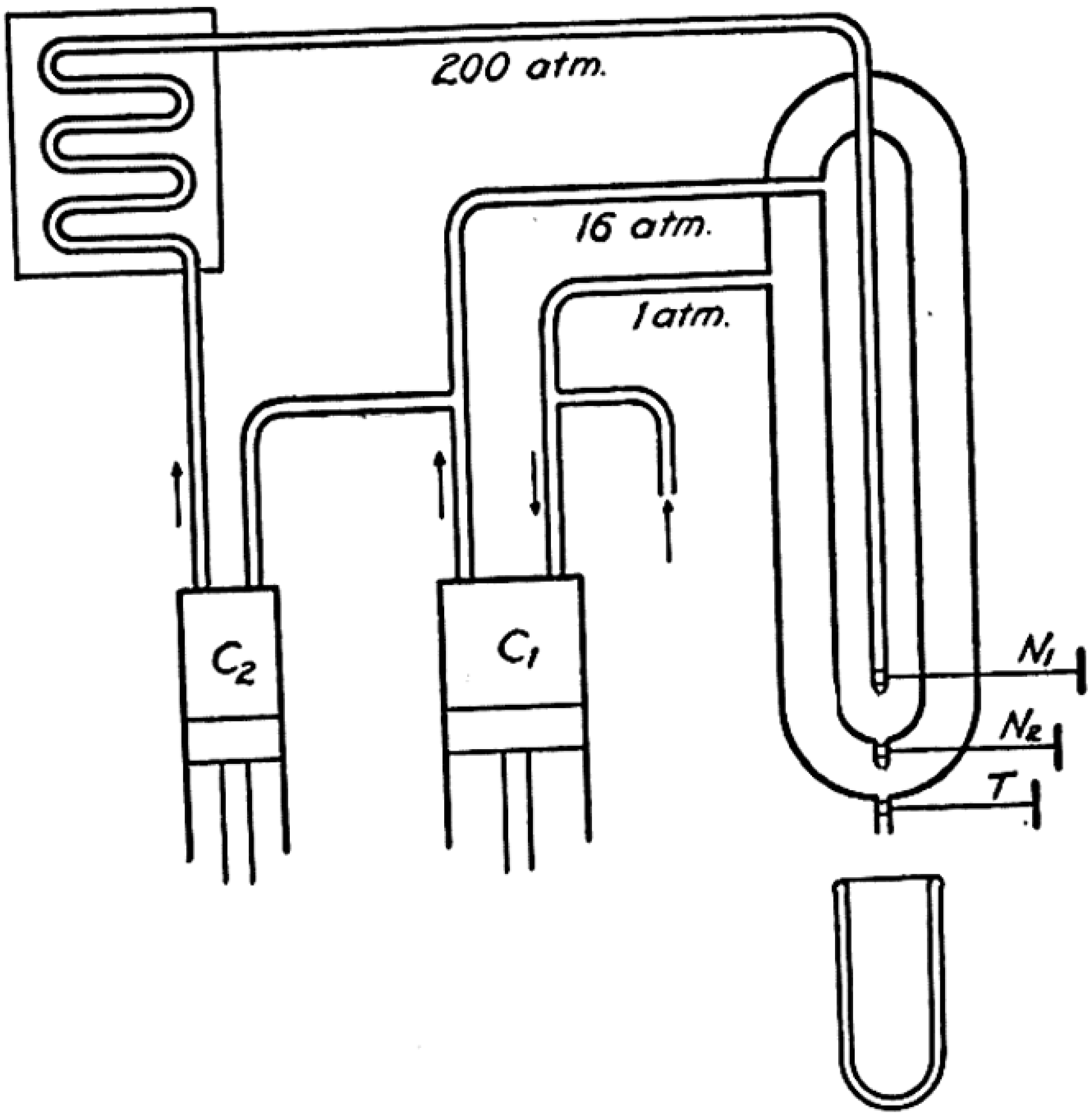

FIG. 126. Liquefaction by the regenerative or Linde process.

progressively the incoming air at a high pressure. The remaining one-fifth of the air expands through the nozzle N_2 to a pressure of 1 atmosphere. This gas passes back through an outer concentric pipe so as to cool still further the incoming gas. After a steady state is reached it will be found that about one-fourth of the gas upon this final expansion is liquefied and may be drawn off at T.

If hydrogen is subjected to these same pressures and allowed to expand, it will show a progressive warming rather than cooling. However, if it be supercooled below about −80° C. it behaves upon throttling in a manner similar to air. Kammerlingh Onnes[11] successfully employed the method to liquefy helium in 1908. In this investigation the compressed helium before throttling was supercooled by passing it through a chamber containing liquid hydrogen boiling at a reduced pressure so that its temperature was 15° K.

Liquefaction of Helium by Adiabatic Expansion, Simon. An exceedingly simple device capable of producing small quantities of liquid helium has been described by Simon[12] and accepted in practice in many[13] cryogenic laboratories. The arrangement of the apparatus is as shown in Fig. 127. The hydrogen bath *E* at a temperature of about 10° K. cools the gaseous helium as it is compressed in the bulb *B* to about 150 atmospheres. The space *D*, originally filled with helium gas to make good thermal contact between bulb *B* and the bath *E* is evacuated thereby leaving the compressed helium gas in bulb *B* thermally insulated. The surrounding space *C* contains helium gas under low pressure serving as a gas thermometer to indicate the temperature. The pressure in bulb *B* is now slowly released and owing to the excellent thermal insulation, the energy needed to do the external work is given up by the compressed helium. When the temperature is reduced below 5° K. at a suitable pressure, liquefaction will occur to the extent that as much as 80 per cent of the volume is filled with liquid helium.

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[11] H. Kammerlingh Onnes, *Comm. Univ. Leiden*, **108**, 1908.

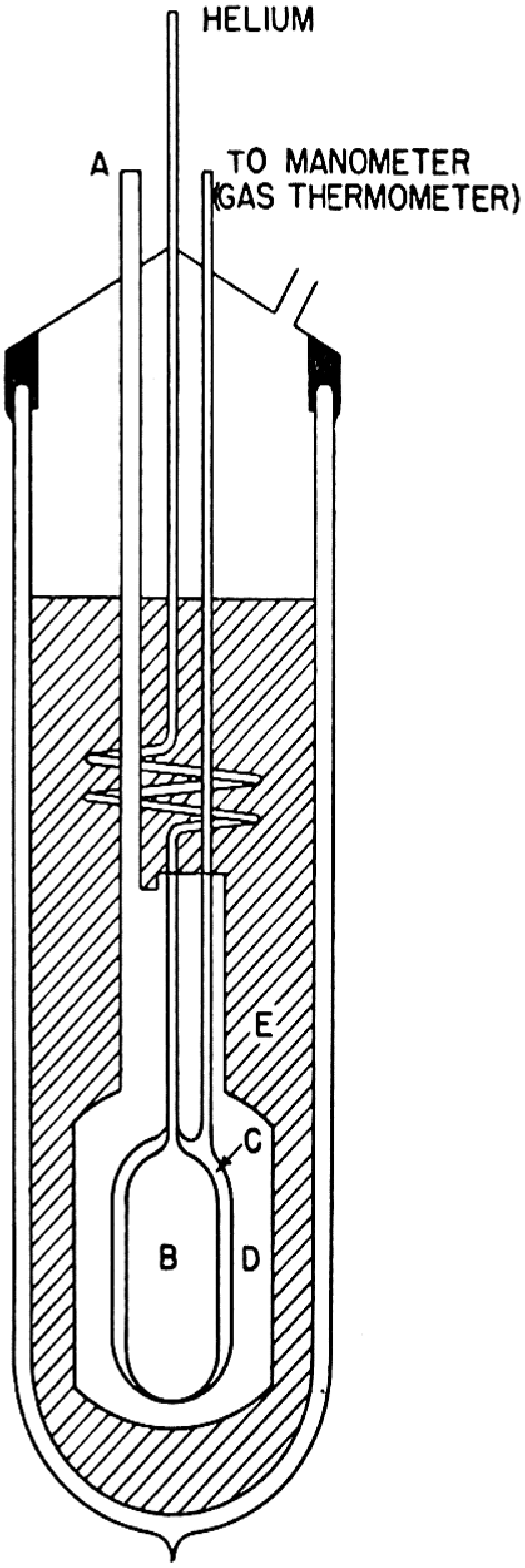

FIG. 127. Apparatus for the liquefaction of helium.

An adaptation of this principle allowing for the continuous liquefaction of gases has been devised by Kapitza.[14] In this apparatus the gas at a very low temperature operates a low pressure turbine in its expansion.

The Solidification of Helium. By starting with a sufficient quantity of any liquid in a thermally insulated container, provided with facilities for maintaining a sufficiently low pressure above the liquid, it is possible to attain the temperature of the triple point of the substance. At this point the liquid freezes. The operation may often be carried further, ending with a subliming solid at a temperature considerably below that of the triple point.

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[12] F. Simon, *Phys. Zeit.*, **27**, 790 (1926).

[13] K. Mendelssohn, *Zeit. Phys.*, **73**, 482 (1931); F. A. Lindemann and T. C. Keeley, *Nature*, **131**, 191 (1933).

[14] P. Kapitza, *Jour. Physics, U.S.S.R.*, **1**, 7 (1939).

In this way, Dewar[15] was able in 1899 to solidify hydrogen, obtaining a porous solid having a density of about 0.07 gm. per cm.^{3} Before the year 1926, the only substance not reducible to the solid state was helium. Kammerlingh Onnes[16] with all the excellent equipment of his cryogenic laboratory, had made repeated attempts to accomplish this end, without success. In his last attempt, liquid helium contained in a flask immersed in boiling hydrogen was exposed to a pressure of 0.013 mm. maintained by operating several rapid pumps in parallel. The temperature of the boiling helium was reduced to perhaps 0.82° K., but no trace of solid helium was observed. The conclusion was drawn that helium would remain liquid even at the absolute zero.

In the same laboratory, however, Keesom[17] in 1926 successfully attained the long-sought objective. The conditions under which success was met were very different from those employed by Kammerlingh Onnes. The explanation may be readily seen from Fig. 81, representing equilibrium conditions between the liquid and solid phases for substances that contract on freezing.

By arranging concentric Dewar flasks containing liquid helium, so that the pressure above the helium could be adjusted to any particular value the desired result could be accomplished. By reducing the pressure in the outer flask the temperature of the whole system can be reduced to a value close to the absolute zero. Now by increasing the pressure above the helium in the inner flask the solid state is attained. The higher the pressure the higher may be the temperature at which the transformation occurs, thus pressures of 25, 50, 100, 1,000, and 5,000 atmospheres give freezing temperatures of 1.2°, 2.4°, 3.5°, 13.5°, and 39° K., respectively. The solid has been found[18] to be characterized by a close packed hexagonal arrangement of atoms, similar to beryllium and magnesium.

The Production of Extremely Low Temperatures by the Demagnetization of Paramagnetic Substances. It was suggested by Debye[19] in 1926 and experimentally demonstrated both by Giauque and MacDougall[20] in California and by deHaas[21] in Leiden in 1933 that temperatures very near the absolute zero might be attained by utilizing the

[15] Sir James Dewar, *Nature*, **60**, 514 (1899).

[16] H. Kammerlingh Onnes, *Comm. Univ. Leiden*, **159**, 1922.

[17] W. H. Keesom, *Comm. Univ. Leiden*, **184b**, 1926.

[18] W. H. Keesom and K. W. Taconis, *Physica*, **5**, 161 (1938).

[19] P. Debye, *Ann. Physik*, **81**, 1154 (1926).

[20] W. F. Giauque and D. P. MacDougall, *Phys. Rev.*, **43**, 768 (1933).

[21] W. J. deHaas, *Nature*, **132**, 372, *et seq.* (1933).

magnetic behavior of certain substances. To magnetize a body a quantity of energy must be added which is proportional to the product of the field strength and the magnetization produced. If the body is thermally insulated, this addition of energy would result in an increase in temperature. Conversely, if the paramagnetic substance be magnetized while in contact with a low temperature bath, and then thermally insulated and demagnetized, the temperature would be correspondingly reduced. For those materials which obey the Curie law (i.e., that the susceptibility

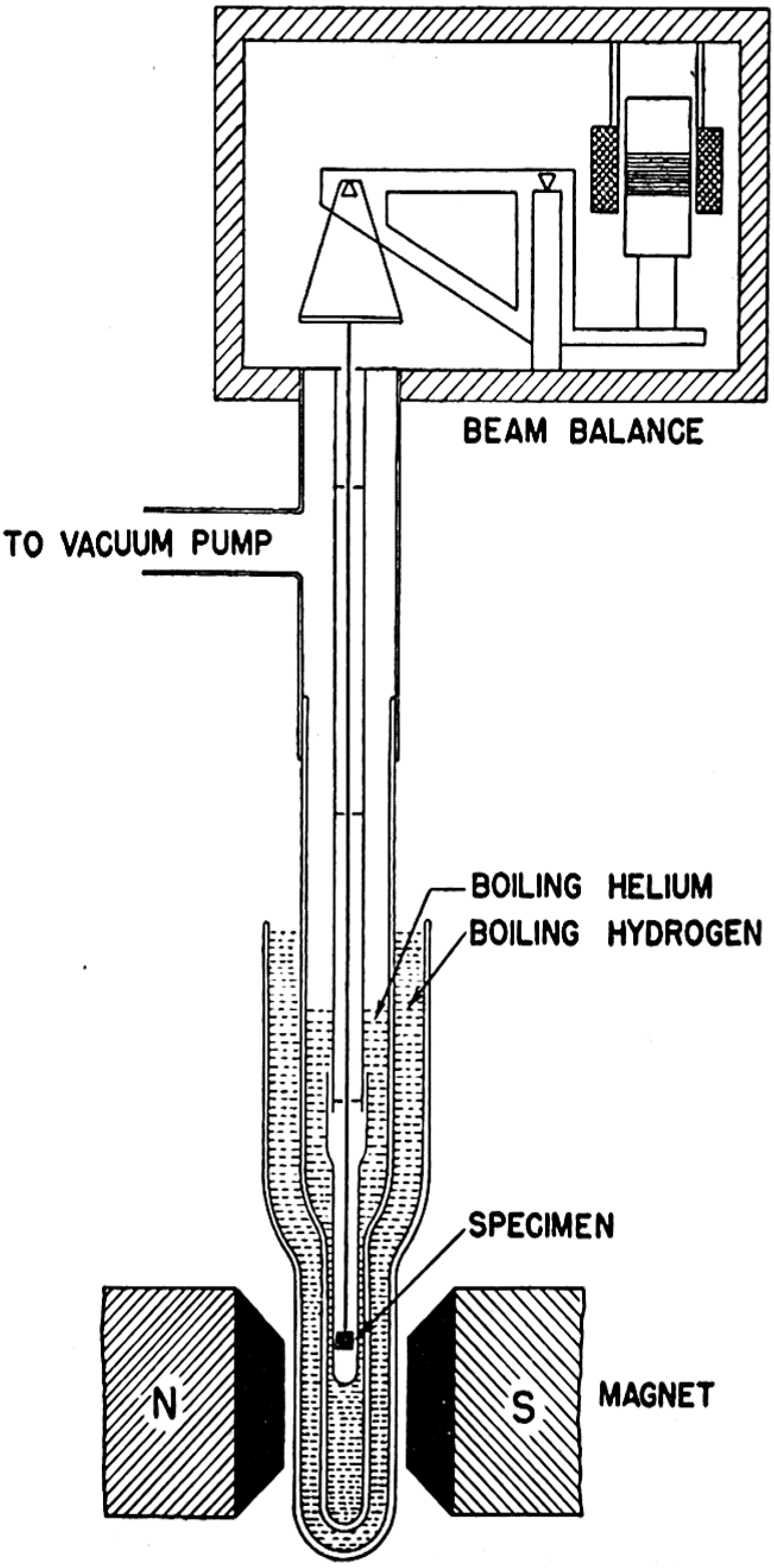

FIG. 128. Apparatus for the production and measurement of extremely low temperatures.

varies inversely with the absolute temperature) at very low temperatures the effect becomes particularly striking.

The arrangement of apparatus is shown schematically in Fig. 128. Helium gas at very low temperatures is an excellent conductor of heat, so that, by surrounding the specimen with this gas, an isothermal connection is made with the outer cryostat of boiling helium as the sample is magnetized. On pumping off the helium the specimen is left thermally insulated. As the magnetic field is reduced the temperature of the specimen falls. By treating a specimen of chrome alum in this way in 1935, deHaas and Wiersma[22] attained a record low temperature of 0.0034° K. They employed a starting field of 24,075 oersteds at a temperature of 1.29° K.

The temperature attained is measured by the same device as shown, in connection with a sensitive dynamometer. The specimen is placed in a position where the magnetic field is nonhomogeneous but of known value as well as of known rate of variation with distance. From the force experienced in this position the susceptibility and hence the temperature may be found, assuming the Curie law to be valid.

[22] W. J. deHaas and E. C. Wiersma, *Physica*, **2**, 235 (1935).

APPENDIX

TABLE 17

SOME FUNDAMENTAL CONSTANTS[1]

Electronic

Charge of electron (e), $(4.8025 \pm 0.0010) \times 10^{-10}$ esu.
$(1.60203 \pm 0.00034) \times 10^{-20}$ emu.

Atomic weight of electron (Aston), 0.00054862
Planck constant (h), $(6.624 \pm 0.002) \times 10^{-27}$ erg sec.

Atomic and Molecular

Mass of hydrogen atom (M_{H}) $(1.67339 \pm 0.00031) \times 10^{-24}$ gm.
Avogadro's number (N), $(6.0228 \pm 0.0011) \times 10^{23}$ per gm-mol.
Loschmidt's number (0° C.) (N), $(2.6870 \pm 0.0005) \times 10^{19}$ per cm.^{3}
Volume of 1 gm-mol. gas (0° C.) 1 atm. P. $(22{,}414 \pm 0.0008) \times 10^3$ cm.^{3}
Gas constant per gm-mol. (R), (1.9864 ± 0.0002) (cal.)$_{15°}$ per deg. per gm-mol.
$(8.3143 \pm 0.0004) \times 10^7$ ergs per deg. per gm-mol.

Gas constant per particle (Boltzmann) (k), $(1.3708 \pm 0.0014) \times 10^{-16}$ erg per deg. per particle.

Thermal

Mechanical equivalent of heat (J), 4.1855 ± 0.0004 absolute joules per cal.$_{15°}$ or 4.1847 ± 0.0003 International joules per cal.$_{15°}$
Solar Constant (S) 1.94 cal. per cm.^{2} per min. or 1.353×10^6 ergs per cm.^{2} per sec.

Radiation

Stefan-Boltzmann constant (σ), $(5.672 \pm 0.003) \times 10^{-5}$ erg cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$
Constant in the Wien and Planck distribution laws (C_2), $(14{,}384 \pm 3)$ micron deg. abs.
Wien displacement constant, (2897.1 ± 0.7) micron deg. abs.
Velocity of radiation (vacuum) (C), $(2.99776 \pm 0.00004) \times 10^{10}$ cm. per sec.

[1] Probable errors as computed by R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

TABLE 18

CONDUCTIVITY OF SOME THERMAL INSULATING MATERIALS IN JOULES CM.$^{-1}$ SEC.$^{-1}$ DEG. C.$^{-1}$

These values vary greatly with thickness of specimen, temperature and dryness.

Material	$\kappa \times 10^3$	Material	$\kappa \times 10^3$
Cork	0.32 → 0.79	Brick	1.8 → 5.2
Paper	0.45 → 0.70	Soil	1.4 → 6.7
Loose hair felt	0.48	Mica	3.6 → 5.9
Diatomite	0.52 → 1.58	Concrete	3.0 → 8.0
Sawdust	0.60	Glass	6.0 → 7.6
Asbestos paper	0.80	Porcelain	10.4
Ash, fine	1.5	Plaster of Paris	3.0 → 11.0
Rubber, sponge	0.35 → 0.40	Limestone	7.0 → 15
Rubber, vulcanized	1.4 → 2.5	Ice	11
Wood (walnut)	1.5 → 3.3	Granite	22
Graphite, powdered	2 → 10		

TABLE 19

VAPOR TENSION OF WATER FROM 0° TO 150° C.

T in deg. C.; *P* in mm. Hg

T	*P*	*T*	*Pmm*	*T*	*P*	*T*	*P*	*T*	*P*	*T*	*P*
1	4.909	26	24.956	51	96.664	76	301.09	101	787.59	126	1798.35
2	5.271	27	26.471	52	101.55	77	313.85	102	816.01	127	1854.20
3	5.658	28	28.065	53	106.65	78	327.05	103	845.28	128	1911.47
4	5.069	29	29.744	54	111.97	79	340.73	104	875.41	129	1970.15
5	6.507	30	31.510	55	117.52	80	354.87	105	906.41	130	2030.28
6	6.972	31	33.366	56	123.29	81	369.51	106	938.31	131	2091.94
7	7.466	32	35.318	57	129.31	82	384.64	107	971.14	132	2155.03
8	7.991	33	32.369	58	135.58	83	400.29	108	1004.91	133	2219.69
9	8.548	34	39.523	59	142.10	84	416.47	109	1039.65	134	2285.92
10	9.140	35	41.784	60	148.88	85	433.19	110	1075.37	135	2353.73
11	9.767	36	44.158	61	155.95	86	450.47	111	1112.09	136	2423.16
12	10.432	37	46.648	62	163.29	87	468.32	112	1149.83	137	2494.23
13	11.137	38	49.259	63	170.92	88	486.76	113	1188.61	138	2567.00
14	11.884	39	51.797	64	178.86	89	505.81	114	1228.47	139	2641.44
15	12.674	40	54.865	65	187.10	90	525.47	115	1269.41	140	2717.63
16	13.510	41	57.870	66	195.67	91	547.77	116	1311.47	141	2795.57
17	14.395	42	61.017	67	204.56	92	566.71	117	1354.66	142	2875.30
18	15.330	43	64.310	68	213.79	93	588.33	118	1399.02	143	2956.86
19	16.319	44	67.757	69	223.37	94	610.64	119	1444.55	144	3040.26
20	17.363	45	71.362	70	233.31	95	633.66	120	1491.28	145	3125.55
21	18.466	46	75.131	71	243.62	96	657.40	121	1539.25	146	3212.74
22	19.630	47	79.071	72	254.30	97	681.88	122	1588.47	147	3301.87
23	20.858	48	83.188	73	265.38	98	707.13	123	1638.96	148	3392.98
24	22.152	49	87.488	74	276.87	99	733.16	124	1690.76	149	3486.09
25	23.517	50	91.978	75	288.76	100	760.00	125	1743.88	150	3581.21

TABLE 20

E.M.F. TEMPERATURE RELATIONSHIP FOR THERMOCOUPLE OF IRON-CONSTANTAN. COLD JUNCTION AT 0° C.

Deg. C.	0°	100°	200°	300°	400°	500°
	Millivolts					
0°	0.0	5.28	10.78	16.30	21.82	27.39
2°	0.10	5.39	10.89	16.41	21.93	27.50
4°	0.21	5.50	11.00	16.52	22.04	27.62
6°	0.31	5.61	11.11	16.63	22.15	27.73
8°	0.42	5.72	11.22	16.74	22.26	27.84
10°	0.52	5.83	11.33	16.85	22.37	27.96
12°	0.62	5.94	11.44	16.96	22.48	28.08
14°	0.73	6.05	11.55	17.07	22.59	28.19
16°	0.83	6.16	11.66	17.18	22.70	28.31
18°	0.94	6.27	11.77	17.29	22.81	28.42
20°	1.04	6.38	11.88	17.40	22.92	28.53
22°	1.14	6.49	11.99	17.51	23.03	28.65
24°	1.25	6.60	12.10	17.62	23.14	28.76
26°	1.35	6.70	12.22	17.74	23.26	28.88
28°	1.46	6.81	12.33	17.85	23.37	28.99
30°	1.56	6.92	12.44	17.96	23.48	29.11
32°	1.66	7.03	12.55	18.07	23.59	29.22
34°	1.77	7.14	12.66	18.18	23.70	29.33
36°	1.87	7.25	12.77	18.29	23.81	29.45
38°	1.98	7.36	12.88	18.40	23.92	29.56
40°	2.08	7.47	12.99	18.51	24.03	29.68
42°	2.18	7.58	13.10	18.62	24.14	29.79
44°	2.29	7.69	13.21	18.73	24.25	29.91
46°	2.39	7.80	13.32	18.84	24.36	30.02
48°	2.50	7.91	13.43	18.95	24.47	30.14
50°	2.60	8.02	13.54	19.06	24.58	30.25
52°	2.71	8.13	13.65	19.17	24.69	30.37
54°	2.81	8.24	13.76	19.28	24.80	30.48
56°	2.92	8.35	13.87	19.39	24.92	30.60
58°	3.03	8.46	13.98	19.50	25.03	30.71
60°	3.14	8.57	14.09	19.61	25.14	30.83
62°	3.24	8.68	14.20	19.72	25.25	30.95
64°	3.35	8.79	14.31	19.83	25.37	31.06
66°	3.46	8.90	14.42	19.94	25.48	31.18
68°	3.56	9.01	14.53	20.05	25.59	31.30
70°	3.67	9.12	14.64	20.16	25.70	31.41
72°	3.78	9.23	14.75	20.27	25.82	31.53
74°	3.89	9.34	14.86	20.38	25.93	31.65
76°	3.99	9.45	14.98	20.49	26.04	31.76
78°	4.10	9.57	15.09	20.61	26.15	31.88
80°	4.21	9.68	15.20	20.72	26.27	32.00
82°	4.31	9.79	15.31	20.83	26.38	32.11
84°	4.42	9.90	15.42	20.94	26.49	32.23
86°	4.53	10.01	15.53	21.05	26.60	32.35
88°	4.64	10.12	15.64	21.16	26.72	32.46
90°	4.74	10.23	15.75	21.27	26.83	32.58
92°	4.85	10.34	15.86	21.38	26.94	32.69
94°	4.96	10.45	15.97	21.49	27.05	32.81
96°	5.06	10.56	16.08	21.60	27.17	32.93
98°	5.17	10.67	16.19	21.71	27.28	33.04
100°	5.28	10.78	16.30	21.82	27.39	33.16
M.V. per deg. C.	0.0528	0.055	0.0552	0.0552	0.0557	0.0577

TABLE 20 (*Continued*)

Deg. C.	600°	700°	800°	900°	1000°
	Millivolts				
0°	33.16	39.19	45.48	51.82	58.16
2°	33.28	39.32	45.61	51.95	58.29
4°	33.40	39.44	45.73	52.07	58.41
6°	33.52	39.57	45.86	52.20	58.54
8°	33.64	39.69	45.99	52.33	58.67
10°	33.75	39.82	46.11	52.45	58.79
12°	33.87	39.94	46.24	52.58	58.92
14°	33.99	40.07	46.37	52.71	59.05
16°	34.11	40.19	46.49	52.83	59.17
18°	34.23	40.32	46.62	52.96	59.30
20°	34.35	40.44	46.75	53.09	59.43
22°	34.47	40.57	46.87	53.21	59.55
24°	34.59	40.69	47.00	53.34	59.68
26°	34.70	40.82	47.13	53.47	59.81
28°	34.82	40.94	47.26	53.60	59.94
30°	34.94	41.07	47.38	53.72	60.06
32°	35.06	41.19	47.51	53.85	60.19
34°	35.18	41.32	47.64	53.98	60.32
36°	35.30	41.44	47.76	54.10	60.44
38°	35.42	41.57	47.89	54.23	60.57
40°	35.54	41.69	48.02	54.36	60.70
42°	35.65	41.82	48.14	54.48	60.82
44°	35.77	41.94	48.27	54.61	60.95
46°	35.89	42.07	48.40	54.74	61.08
48°	36.01	42.19	48.52	54.86	61.20
50°	36.13	42.32	48.65	54.99	61.33
52°	36.25	42.45	48.78	55.12	61.46
54°	36.37	42.57	48.90	55.24	61.58
56°	36.50	42.70	49.03	55.37	61.71
58°	36.62	42.83	49.16	55.50	61.84
60°	36.74	42.95	49.28	55.62	61.96
62°	36.86	43.08	49.41	55.75	62.09
64°	36.99	43.20	49.54	55.88	62.22
66°	37.11	43.33	49.66	56.00	62.34
68°	37.23	43.46	49.79	56.13	62.47
70°	37.35	43.58	49.92	56.26	62.60
72°	37.48	43.71	50.04	56.38	62.72
74°	37.60	43.84	50.17	56.51	62.85
76°	37.72	43.96	50.30	56.64	62.98
78°	37.84	44.09	50.43	56.77	63.10
80°	37.97	44.22	50.55	56.89	63.23
82°	38.09	44.34	50.68	57.02	63.36
84°	38.21	44.47	50.80	57.16	63.49
86°	38.33	44.60	50.92	57.27	63.61
88°	38.46	44.72	51.06	57.40	63.74
90°	38.58	44.85	51.19	57.53	63.87
92°	38.70	44.97	51.31	57.65	63.99
94°	38.82	45.10	51.44	57.78	64.12
96°	38.94	45.23	51.57	57.91	64.25
98°	39.07	45.35	51.69	58.03	64.37
100°	39.19	45.48	51.82	58.16	64.50
M.V. per deg. C.	0.0603	0.0629	0.0634	0.0634	0.0634

TABLE 21

Chromel vs. Alumel Thermocouple

(Degrees centigrade; reference junction 0° C.)

° C.	0°	100°	200°	300°	400°	500°	600°
	Millivolts						
0	0	4.10	8.13	12.21	16.39	20.64	24.90
2	0.08	4.18	8.21	12.29	16.47	20.73	24.99
4	0.16	4.26	8.29	12.37	16.55	20.81	25.07
6	0.24	4.34	8.37	12.45	16.64	20.90	25.16
8	0.32	4.42	8.45	12.53	16.73	20.98	25.24
10	0.40	4.51	8.53	12.62	16.82	21.07	25.33
12	0.48	4.59	8.61	12.70	16.90	21.15	25.41
14	0.56	4.67	8.69	12.78	16.99	21.24	25.50
16	0.64	4.75	8.77	12.86	17.07	21.32	25.58
18	0.72	4.83	8.85	12.95	17.16	21.41	25.67
20	0.80	4.92	8.93	13.04	17.24	21.49	25.75
22	0.88	5.00	9.01	13.12	17.32	21.58	25.84
24	0.96	5.08	9.09	13.20	17.41	21.66	25.93
26	1.04	5.16	9.17	13.28	17.49	21.75	26.01
28	1.12	5.24	9.25	13.36	17.58	21.83	26.09
30	1.20	5.33	9.34	13.45	17.66	21.92	26.18
32	1.28	5.41	9.42	13.53	17.74	22.00	26.26
34	1.36	5.49	9.50	13.61	17.83	22.09	26.35
36	1.44	5.57	9.58	13.69	17.91	22.17	26.43
38	1.52	5.65	9.66	13.78	18.00	22.26	26.52
40	1.61	5.73	9.74	13.87	18.08	22.34	26.60
42	1.69	5.81	9.82	13.95	18.16	22.43	26.69
44	1.77	5.89	9.90	14.03	18.25	22.52	26.77
46	1.85	5.97	9.98	14.11	18.33	22.60	26.86
48	1.93	6.05	10.06	14.20	18.42	22.68	26.94
50	2.02	6.13	10.15	14.29	18.50	22.77	27.03
52	2.10	6.21	10.23	14.37	18.58	22.86	27.12
54	2.18	6.29	10.31	14.45	18.66	22.94	27.20
56	2.26	6.37	10.39	14.53	18.75	23.03	27.28
58	2.34	6.45	10.47	14.62	18.84	23.11	27.37
60	2.43	6.53	10.56	14.71	18.93	23.20	27.45
62	2.51	6.61	10.64	14.79	19.02	23.28	27.53
64	2.59	6.69	10.72	14.88	19.11	23.37	27.62
66	2.67	6.77	10.80	14.96	19.20	23.45	27.70
68	2.76	6.85	10.88	15.05	19.28	23.54	27.79
70	2.85	6.93	10.97	15.13	19.36	23.62	27.87
72	2.93	7.01	11.05	15.21	19.44	23.71	27.95
74	3.01	7.09	11.13	15.30	19.53	23.79	28.04
76	3.09	7.17	11.21	15.38	19.61	23.88	28.12
78	3.17	7.25	11.29	15.47	19.70	23.96	28.21
80	3.26	7.33	11.38	15.55	19.78	24.05	28.29
82	3.34	7.41	11.46	15.63	19.87	24.14	28.38
84	3.42	7.49	11.54	15.72	19.95	24.22	28.46
86	3.50	7.57	11.62	15.80	20.04	24.31	28.55
88	3.59	7.65	11.71	15.89	20.12	24.39	28.63
90	3.68	7.73	11.80	15.97	20.21	24.48	28.72
92	3.76	7.81	11.88	16.05	20.30	24.56	28.80
94	3.84	7.89	11.96	16.14	20.38	24.65	28.89
96	3.92	7.97	12.04	16.22	20.47	24.73	28.97
98	4.01	8.05	12.12	16.31	20.55	24.82	29.06
100	4.10	8.13	12.21	16.39	20.64	24.90	29.14
Millivolts per ° C.	0.041	0.0403	0.0408	0.0418	0.0425	0.0426	0.0424

TABLE 21 (*Continued*)

° C.	700°	800°	900°	1000°	1100°	1200°	1300°
	Millivolts						
0	29.14	33.31	37.36	41.31	45.14	48.85	52.41
2	29.22	33.39	37.44	41.39	45.22	48.93	52.48
4	29.31	33.47	37.52	41.47	45.29	49.00	52.55
6	29.39	33.55	37.60	41.55	45.37	49.07	52.62
8	29.48	33.63	37.68	41.63	45.44	49.14	52.69
10	29.56	33.71	37.76	41.70	45.52	49.21	52.75
12	29.64	33.79	37.84	41.78	45.59	49.29	52.82
14	29.73	33.87	37.92	41.86	45.67	49.36	52.89
16	29.81	33.95	38.00	41.94	45.74	49.43	52.96
18	29.90	34.03	38.08	42.01	45.82	49.50	53.03
20	29.98	34.12	38.16	42.08	45.89	49.57	53.10
22	30.06	34.20	38.24	42.16	45.97	49.65	53.17
24	30.15	34.28	38.32	42.24	46.04	49.73	53.24
26	30.23	34.36	38.40	42.32	46.12	49.80	53.31
28	30.32	34.44	38.48	42.40	46.19	49.87	53.38
30	30.40	34.53	38.56	42.47	46.27	49.94	53.45
32	30.48	34.61	38.64	42.55	46.35	50.01	53.52
34	30.57	34.69	38.72	42.62	46.43	50.08	53.59
36	30.65	34.77	38.80	42.70	46.50	50.15	53.66
38	30.74	34.85	38.88	42.78	46.57	50.22	53.73
40	30.82	34.94	38.96	42.86	46.64	50.29	53.79
42	30.90	35.02	39.04	42.94	46.71	50.37	53.86
44	30.98	35.10	39.12	43.02	46.79	50.44	53.93
46	31.06	35.18	39.20	43.10	46.86	50.51	54.00
48	31.14	35.26	39.28	43.17	46.94	50.58	54.07
50	31.23	35.35	39.35	43.24	47.01	50.65	54.13
52	31.31	35.43	39.43	43.32	47.08	50.72	54.20
54	31.40	35.51	39.51	43.39	47.16	50.79	54.27
56	31.48	35.59	39.59	43.47	47.23	50.86	54.34
58	31.57	35.67	39.67	43.54	47.31	50.93	54.41
60	31.65	35.75	39.75	43.62	47.38	51.00	54.47
62	31.73	35.83	39.83	43.70	47.45	51.08	54.54
64	31.82	35.91	39.91	43.77	47.53	51.15	54.61
66	31.90	35.99	39.99	43.85	47.60	51.22	54.68
68	31.99	36.07	40.07	43.92	47.68	51.29	54.75
70	32.07	36.16	40.14	44.00	47.75	51.36	54.81
72	32.15	36.24	40.22	44.08	47.82	51.43	54.88
74	32.23	36.32	40.30	44.15	47.90	41.50	54.95
76	32.31	36.40	40.38	44.23	47.97	51.57	55.02
78	32.39	36.48	40.46	44.30	48.05	51.64	55.09
80	32.48	36.56	40.53	44.38	48.12	51.71	55.15
82	32.56	36.64	40.61	44.46	48.20	51.78	55.22
84	32.65	36.72	40.69	44.53	48.27	51.85	55.29
86	32.73	36.80	40.77	44.61	48.34	51.92	55.36
88	32.82	36.88	40.85	44.68	48.41	51.99	55.42
90	32.90	36.96	40.92	44.76	48.48	52.06	55.48
92	32.98	37.04	41.00	44.84	48.56	52.13	55.55
94	33.06	37.12	41.08	44.91	48.64	52.20	55.62
96	33.14	37.20	41.16	44.99	48.71	52.27	55.69
98	33.22	37.28	41.24	45.06	48.78	52.34	55.75
100	33.31	37.36	41.31	45.14	48.85	52.41	55.81
Millivolts per ° C.	0.0417	0.0405	0.0395	0.0383	0.0371	0.0356	0.0340

TABLE 22

PLATINUM VS. PLATINUM + 10 PER CENT RHODIUM THERMOCOUPLE

(Degrees centigrade; reference junction 0° C.)

° C.	0°	100°	200°	300°	400°	500°	600°	700°	800°
	Millivolts								
0	0	0.643	1.436	2.316	3.251	4.219	5.222	6.260	7.330
2	0.011	0.658	1.453	2.334	3.270	4.239	5.243	6.281	7.352
4	0.023	0.672	1.470	2.352	3.289	4.258	5.263	6.302	7.374
6	0.034	0.687	1.487	2.370	3.308	4.278	5.284	6.323	7.396
8	0.046	0.702	1.504	2.388	3.327	4.298	5.304	6.344	7.417
10	0.057	0.717	1.521	2.406	3.346	4.318	5.325	6.365	7.439
12	0.068	0.732	1.538	2.425	3.365	4.337	5.345	6.387	7.461
14	0.080	0.747	1.555	2.443	3.384	4.357	5.366	6.408	7.483
16	0.091	0.762	1.572	2.462	3.403	4.377	5.386	6.429	7.505
18	0.103	0.777	1.589	2.480	3.422	4.397	5.407	6.450	7.527
20	0.114	0.792	1.606	2.498	3.441	4.417	5.427	6.471	7.548
22	0.126	0.807	1.623	2.517	3.461	4.436	5.448	6.493	7.570
24	0.138	0.822	1.641	2.536	3.480	4.456	5.469	6.514	7.592
26	0.150	0.838	1.658	2.554	3.499	4.476	5.489	6.535	7.614
28	0.162	0.853	1.675	2.573	3.519	4.496	5.510	6.556	7.636
30	0.174	0.869	1.692	2.591	3.538	4.516	5.530	6.578	7.658
32	0.186	0.884	1.710	2.610	3.557	4.536	5.551	6.599	7.680
34	0.198	0.899	1.727	2.628	3.577	4.556	5.571	6.620	7.702
36	0.211	0.915	1.744	2.647	3.596	4.576	5.592	6.642	7.724
38	0.223	0.931	1.762	2.665	3.615	4.596	5.613	6.663	7.746
40	0.235	0.946	1.779	2.684	3.634	4.616	5.633	6.684	7.768
42	0.248	0.962	1.797	2.703	3.653	4.636	5.654	6.706	7.790
44	0.260	0.977	1.814	2.721	3.673	4.656	5.675	6.727	7.812
46	0.273	0.993	1.832	2.740	3.692	4.676	5.696	6.748	7.834
48	0.286	1.009	1.850	2.759	3.711	4.696	5.717	6.769	7.856
50	0.299	1.025	1.867	2.778	3.731	4.716	5.737	6.790	7.878
52	0.312	1.041	1.885	2.796	3.750	4.736	6.758	6.812	7.900
54	0.325	1.057	1.902	2.815	3.770	4.756	5.779	6.834	7.922
56	0.338	1.073	1.920	2.834	3.789	4.776	5.800	6.855	7.944
58	0.351	1.089	1.938	2.852	3.808	4.796	5.821	6.877	7.966
60	0.365	1.105	1.956	2.871	3.828	4.817	5.841	6.898	7.989
62	0.378	1.121	1.973	2.890	3.847	4.837	5.862	6.920	8.011
64	0.391	1.137	1.991	2.909	3.867	4.857	5.883	6.941	8.033
66	0.405	1.154	2.009	2.928	3.886	4.877	5.904	6.963	8.055
68	0.418	1.170	2.027	2.947	3.906	4.897	5.925	6.984	8.077
70	0.432	1.186	2.045	2.965	3.925	4.918	5.945	7.005	8.100
72	0.445	1.203	2.063	2.984	3.945	4.938	5.966	7.027	8.122
74	0.459	1.219	2.081	3.003	3.964	4.958	5.987	7.049	8.144
76	0.473	1.236	2.099	3.022	3.984	4.978	6.008	7.070	8.166
78	0.487	1.252	2.117	3.041	4.003	4.998	6.029	7.092	8.188
80	0.500	1.269	2.134	3.060	4.023	5.019	6.050	7.113	8.211
82	0.514	1.285	2.152	3.079	4.042	5.039	6.071	7.135	8.233
84	0.528	1.302	2.170	3.098	4.062	5.059	6.092	7.157	8.255
86	0.542	1.318	2.189	3.117	4.081	5.080	6.113	7.179	8.277
88	0.557	1.335	2.207	3.136	4.101	5.100	6.134	7.200	8.300
90	0.571	1.352	2.225	3.155	4.121	5.120	6.155	7.222	8.322
92	0.585	1.368	2.243	3.174	4.140	5.141	6.176	7.244	8.344
94	0.600	1.385	2.261	3.193	4.160	5.161	6.197	7.265	8.367
96	0.614	1.402	2.279	3.212	4.180	5.182	6.218	7.287	8.389
98	0.629	1.419	2.297	3.232	4.200	5.202	6.239	7.309	8.411
100	0.643	1.436	2.316	3.251	4.219	5.222	6.260	7.330	8.434
Millivolts per ° C.	0.00643	0.00793	0.00880	0.00935	0.00968	0.0100	0.0104	0.0107	0.0110

TABLE 22 (*Continued*)

° C.	900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°	1700°
	Millivolts								
0	8.434	9.569	10.736	11.924	13.120	14.312	15.498	16.674	17.841
2	8.456	9.592	10.759	11.948	13.144	14.336	15.521	16.698	17.864
4	8.479	9.615	10.783	11.972	13.168	14.360	15.545	16.721	17.887
6	8.501	9.638	10.807	11.995	13.192	14.383	15.569	16.744	17.910
8	8.523	9.661	10.830	12.019	13.216	14.407	15.592	16.768	17.934
10	8.546	9.685	10.854	12.043	13.239	14.431	15.615	16.792	17.957
12	8.568	9.708	10.878	12.067	13.263	14.455	15.639	16.815	17.980
14	8.591	9.731	10.901	12.091	13.287	14.479	15.663	16.838	18.004
16	8.613	9.754	10.925	12.115	13.311	14.502	15.687	16.861	18.027
18	8.636	9.777	10.949	12.139	13.335	14.526	15.710	16.885	18.050
20	8.658	9.800	10.973	12.163	13.358	14.550	15.733	16.908	18.073
22	8.681	9.823	10.996	12.187	13.382	14.574	15.757	16.932	
24	8.703	9.846	11.020	12.211	13.406	14.597	15.781	16.955	
26	8.726	9.869	11.044	12.235	13.430	14.621	15.805	16.978	
28	8.748	9.893	11.067	12.259	13.454	14.645	15.828	17.002	
30	8.771	9.916	11.091	12.283	13.478	14.668	15.852	17.026	
32	8.794	9.939	11.115	12.307	13.502	14.692	15.875	17.049	
34	8.816	9.962	11.139	12.330	13.526	14.716	15.899	17.072	
36	8.839	9.985	11.162	12.354	13.550	14.740	15.923	17.095	
38	8.861	10.009	11.186	12.378	13.574	14.764	15.946	17.119	
40	8.884	10.033	11.209	12.402	13.598	14.787	15.969	17.142	
42	8.907	10.056	11.233	12.426	13.621	14.811	15.993	17.165	
44	8.929	10.079	11.257	12.450	13.645	14.835	16.017	17.189	
46	8.952	10.102	11.281	12.474	13.669	14.859	16.040	17.212	
48	8.975	10.125	11.305	12.498	13.693	14.882	16.064	17.235	
50	8.998	10.149	11.329	12.522	13.717	14.906	16.087	17.259	
52	9.020	10.172	11.352	12.546	13.741	14.930	16.111	17.282	
54	9.043	10.195	11.376	12.570	13.765	14.953	16.135	17.305	
56	9.066	10.219	11.400	12.594	13.788	14.977	16.158	17.329	
58	9.088	10.242	11.424	12.618	13.812	15.001	16.182	17.352	
60	9.111	10.266	11.448	12.642	13.836	15.024	16.205	17.376	
62	9.134	10.289	11.471	12.666	13.860	15.048	16.229	17.399	
64	9.157	10.313	11.495	12.690	13.884	15.072	16.252	17.422	
66	9.180	10.336	11.519	12.714	13.907	15.096	16.276	17.445	
68	9.202	10.359	11.543	12.738	13.931	15.119	16.299	17.468	
70	9.225	10.383	11.567	12.762	13.955	15.143	16.322	17.492	
72	9.248	10.406	11.590	12.785	13.979	15.167	16.346	17.515	
74	9.271	10.430	11.614	12.809	14.003	15.190	16.369	17.538	
76	9.294	10.453	11.638	12.833	14.026	15.214	16.393	17.562	
78	9.317	10.476	11.662	12.857	14.050	15.237	16.416	17.585	
80	9.340	10.500	11.686	12.881	14.074	15.261	16.440	17.608	
82	9.362	10.524	11.709	12.905	14.098	15.285	16.463	17.631	
84	9.385	10.547	11.733	12.929	14.122	15.308	16.487	17.655	
86	9.408	10.571	11.757	12.953	14.145	15.332	16.510	17.678	
88	9.431	10.594	11.781	12.977	14.169	15.356	16.533	17.701	
90	9.454	10.618	11.805	13.000	14.193	15.379	16.557	17.724	
92	9.477	10.641	11.828	13.024	14.217	15.403	16.580	17.748	
94	9.500	10.665	11.852	13.048	14.241	15.427	16.604	17.771	
96	9.523	10.689	11.876	13.072	14.264	15.450	16.627	17.794	
98	9.556	10.712	11.900	13.096	14.288	15.474	16.651	17.817	
100	9.569	10.736	11.924	13.120	14.312	15.498	16.674	17.841	
Millivolts per ° C.	0.0114	0.0117	0.0119	0.0120	0.0119	0.0119	0.0118	0.0117	0.0116

TABLE 23

Platinum vs. Platinum – 13 Per Cent Rhodium Thermocouple

(Degrees centigrade; reference junction 0° C.)

° C.	0°	100°	200°	300°	400°	500°	600°	700°	800°
	Millivolts								
0	0.000	0.646	1.464	2.394	3.398	4.454	5.561	6.720	7.927
2	0.011	0.661	1.482	2.414	3.419	4.476	5.583	6.743	7.951
4	0.022	0.676	1.500	2.433	3.439	4.497	5.606	6.767	7.976
6	0.033	0.691	1.518	2.453	3.460	4.519	5.629	6.791	8.000
8	0.044	0.706	1.536	2.472	3.480	4.540	5.652	6.815	8.025
10	0.056	0.721	1.553	2.492	3.501	4.562	5.675	6.839	8.049
12	0.067	0.736	1.570	2.512	3.521	4.583	5.698	6.862	8.073
14	0.079	0.752	1.588	2.531	3.542	4.605	5.721	6.886	8.098
16	0.090	0.767	1.606	2.551	3.563	4.627	5.744	6.910	8.123
18	0.102	0.783	1.624	2.570	3.584	4.649	5.767	6.934	8.148
20	0.113	0.798	1.642	2.590	3.605	4.671	5.790	6.958	8.173
22	0.125	0.813	1.660	2.609	3.626	4.693	5.813	6.981	8.198
24	0.137	0.829	1.678	2.629	3.647	4.715	5.836	7.005	8.222
26	0.149	0.845	1.696	2.649	3.668	4.737	5.859	7.029	8.247
28	0.161	0.861	1.714	2.669	3.689	4.759	5.882	7.053	8.271
30	0.173	0.877	1.733	2.689	3.711	4.781	5.905	7.077	8.296
32	0.185	0.893	1.851	2.709	3.732	4.803	5.928	7.100	8.321
34	0.197	0.909	1.770	2.729	3.753	4.825	5.951	7.124	8.346
36	0.209	0.925	1.788	2.749	3.774	4.847	5.974	7.148	8.371
38	0.221	0.941	1.807	2.769	3.795	4.869	5.997	7.172	8.396
40	0.234	0.957	1.825	2.789	3.816	4.891	6.020	7.196	8.421
42	0.247	0.973	1.844	2.809	3.837	4.913	6.043	7.220	8.446
44	0.259	0.990	1.862	2.829	3.858	4.935	6.066	7.244	8.471
46	0.272	1.006	1.881	2.849	3.879	4.957	6.089	7.268	8.496
48	0.284	1.023	1.899	2.869	3.900	4.979	6.112	7.292	8.521
50	0.297	1.039	1.918	2.889	3.921	5.002	6.135	7.317	8.546
52	0.310	1.055	1.937	2.909	3.942	5.024	6.158	7.341	8.571
54	0.324	1.072	1.955	2.929	3.963	5.046	6.181	7.365	8.596
56	0.337	1.088	1.974	2.949	3.984	5.068	6.204	7.389	8.621
58	0.351	1.105	1.992	2.969	4.005	5.090	6.227	7.413	8.646
60	0.364	1.121	2.011	2.990	4.027	5.113	6.251	7.438	8.671
62	0.377	1.138	2.030	3.010	4.048	5.135	6.274	7.462	8.696
64	0.391	1.154	2.049	3.030	4.069	5.157	6.298	7.487	8.721
66	0.404	1.171	2.068	3.050	4.090	5.179	6.321	7.511	8.746
68	0.418	1.187	2.087	3.070	4.111	5.201	6.345	7.536	8.771
70	0.431	1.204	2.106	3.091	4.133	5.224	6.368	7.560	8.796
72	0.444	1.221	2.125	3.111	4.154	5.246	6.391	7.584	8.821
74	0.458	1.238	2.144	3.132	4.175	5.269	6.415	7.609	8.847
76	0.472	1.255	2.163	3.152	4.196	5.291	6.438	7.633	8.872
78	0.486	1.272	2.182	3.173	4.217	5.314	6.462	7.658	8.898
80	0.500	1.290	2.201	3.193	4.239	5.336	6.485	7.682	8.923
82	0.514	1.307	2.220	3.213	4.260	5.358	6.508	7.706	8.948
84	0.529	1.324	2.239	3.234	4.282	5.381	6.532	7.731	8.973
86	0.543	1.341	2.258	3.254	4.303	5.403	6.555	7.755	8.998
88	0.558	1.358	2.277	3.275	4.325	5.426	6.579	7.780	9.023
90	0.572	1.376	2.297	3.295	4.346	5.448	6.602	7.804	9.049
92	0.587	1.394	2.316	3.316	4.368	5.471	6.626	7.829	9.075
94	0.602	1.411	2.336	3.336	4.389	5.493	6.649	7.853	9.100
96	0.617	1.429	2.355	3.357	4.411	5.516	6.673	7.878	9.126
98	0.632	1.446	2.375	3.377	4.432	5.538	6.696	7.902	9.151
100	0.646	1.464	2.394	3.398	4.454	5.561	6.720	7.927	9.177
Millivolts per ° C.	0.00646	0.00818	0.00930	0.01004	0.01056	0.01107	0.01159	0.01207	0.01250

TABLE 23 (*Continued*)

° C.	900°	1000°	1100°	1200°	1300°	1400°	1500°	1600°
	Millivolts							
0	9.177	10.470	11.811	13.181	14.563	15.940	17.316	18.680
2	9.202	10.496	11.838	13.208	14.591	15.968	17.343	18.707
4	9.228	10.522	11.865	13.236	14.618	15.995	17.371	18.734
6	9.253	10.548	11.892	13.263	14.646	16.023	17.398	18.761
8	9.279	10.574	11.919	13.291	14.673	16.050	17.426	18.788
10	9.304	10.601	11.947	13.318	14.701	16.078	17.453	18.815
12	9.330	10.627	11.974	13.346	14.728	16.105	17.480	18.842
14	9.355	10.654	12.002	13.373	14.756	16.133	17.508	18.869
16	9.381	10.680	12.029	13.401	14.783	16.160	17.535	18.896
18	9.406	10.707	12.057	13.428	14.811	16.188	17.563	18.923
20	9.432	10.733	12.084	13.456	14.838	16.215	17.590	18.951
22	9.458	10.759	12.111	13.483	14.865	16.242	17.617	18.978
24	9.483	10.786	12.138	13.511	14.893	16.270	17.645	19.005
26	9.509	10.813	12.165	13.539	14.920	16.298	17.672	19.032
28	9.534	10.840	12.192	13.567	14.948	16.326	17.700	19.059
30	9.560	10.867	12.219	13.595	14.975	16.354	17.727	19.087
32	9.585	10.894	12.246	13.623	15.002	16.381	17.754	19.114
34	9.611	10.920	12.274	13.650	15.030	16.409	17.782	19.141
36	9.637	10.947	12.301	13.678	15.038	16.437	17.809	19.168
38	9.663	10.973	12.329	13.705	15.086	16.465	17.837	19.195
40	9.689	11.000	12.356	13.733	15.114	16.493	17.864	19.222
42	9.715	11.027	12.383	13.761	15.142	16.521	17.891	19.249
44	9.740	11.054	12.411	13.788	15.169	16.548	17.918	19.276
46	9.766	11.081	12.438	13.816	15.197	16.576	17.945	19.303
48	9.791	11.108	12.466	13.843	15.224	16.603	17.972	19.330
50	9.817	11.135	12.493	13.871	15.252	16.631	18.000	19.357
52	9.843	11.161	12.520	13.898	15.279	16.659	18.027	19.384
54	9.869	11.188	12.548	13.926	15.307	16.686	18.054	19.411
56	9.895	11.215	12.575	13.954	15.334	16.714	18.081	19.438
58	9.921	11.242	12.603	13.982	15.362	16.741	18.108	19.465
60	9.947	11.269	12.630	14.010	15.389	16.769	18.135	19.492
62	9.973	11.296	12.658	14.037	15.417	16.796	18.162	19.519
64	9.999	11.323	12.685	14.065	15.444	16.824	18.189	19.546
66	10.025	11.350	12.713	14.092	15.472	16.851	18.216	19.573
68	10.051	11.377	12.740	14.120	15.499	16.879	18.243	19.600
70	10.078	11.404	12.768	14.147	15.527	16.906	18.271	19.627
72	10.104	11.431	12.796	14.175	15.554	16.933	18.298	19.654
74	10.130	11.458	12.823	14.202	15.582	16.961	18.325	19.681
76	10.156	11.485	12.851	14.230	15.609	16.988	18.352	19.708
78	10.182	11.512	12.878	14.257	15.637	17.016	18.379	19.735
80	10.208	11.540	12.906	14.285	15.664	17.043	18.407	19.762
82	10.234	11.567	12.933	14.312	15.691	17.070	18.434	19.789
84	10.260	11.594	12.961	14.340	15.719	17.098	18.461	19.816
86	10.286	11.621	12.988	14.368	15.747	17.125	18.488	19.843
88	10.312	11.648	13.016	14.396	15.775	17.153	18.515	19.870
90	10.339	11.676	13.043	14.424	15.803	17.180	18.543	19.897
92	10.365	11.703	13.071	14.451	15.830	17.207	18.570	19.924
94	10.391	11.730	13.098	14.479	15.858	17.234	18.598	19.951
96	10.417	11.757	13.126	14.507	15.885	17.261	18.625	19.978
98	10.443	11.784	13.153	14.535	15.913	17.288	18.653	20.005
100	10.470	11.811	13.181	14.563	15.940	17.316	18.680	20.032
Millivolts per ° C.	0.01293	0.01341	0.01370	0.01382	0.01377	0.01376	0.01364	0.01352

TABLE 24

Copper vs. Constantan Thermocouple

(Degrees centigrade; reference junction 0° C.)

° C.	Millivolts	° C.	Millivolts	° C.	Millivolts	° C.	Millivolts	° C.	Millivolts	° C.	Millivolts
0	0.00	50	2.03	100	4.28	150	6.70	200	9.29	250	12.01
1	0.04	51	2.08	101	4.32	151	6.75	201	9.34	251	12.07
2	0.08	52	2.12	102	4.37	152	6.80	202	9.39	252	12.12
3	0.12	53	2.16	103	4.42	153	6.85	203	9.44	253	12.18
4	0.16	54	2.21	104	4.46	154	6.90	204	9.50	254	12.23
5	0.19	55	2.25	105	4.51	155	6.95	205	9.55	255	12.29
6	0.23	56	2.29	106	4.56	156	7.00	206	9.60	256	12.35
7	0.27	57	2.34	107	4.61	157	7.05	207	9.66	257	12.40
8	0.31	58	2.38	108	4.65	158	7.10	208	9.71	258	12.46
9	0.35	59	2.42	109	4.70	159	7.15	209	9.77	259	12.51
10	0.39	60	2.47	110	4.75	160	7.21	210	9.82	260	12.57
11	0.43	61	2.51	111	4.79	161	7.26	211	9.87	261	12.63
12	0.47	62	2.56	112	4.84	162	7.31	212	9.93	262	12.68
13	0.51	63	2.60	113	4.89	163	7.36	213	9.98	263	12.74
14	0.55	64	2.64	114	4.94	164	7.41	214	10.04	264	12.80
15	0.59	65	2.69	115	4.99	165	7.46	215	10.09	265	12.85
16	0.63	66	2.73	116	5.03	166	7.51	216	10.14	266	12.91
17	0.67	67	2.78	117	5.08	167	7.56	217	10.20	267	12.97
18	0.71	68	2.82	118	5.13	168	7.61	218	10.25	268	13.02
19	0.75	69	2.86	119	5.18	169	7.66	219	10.31	269	13.08
20	0.79	70	2.91	120	5.23	170	7.72	220	10.36	270	13.14
21	0.83	71	2.95	121	5.27	171	7.77	221	10.41	271	13.19
22	0.87	72	3.00	122	5.32	172	7.82	222	10.47	272	13.25
23	0.91	73	3.04	123	5.37	173	7.87	223	10.52	273	13.31
24	0.95	74	3.09	124	5.42	174	7.92	224	10.58	274	13.36
25	0.99	75	3.13	125	5.47	175	7.97	225	10.63	275	13.42
26	1.03	76	3.18	126	5.51	176	8.03	226	10.69	276	13.48
27	1.07	77	3.22	127	5.56	177	8.08	227	10.74	277	13.54
28	1.11	78	3.27	128	5.61	178	8.13	228	10.80	278	13.59
29	1.15	79	3.31	129	5.66	179	8.18	229	10.85	279	13.65
30	1.19	80	3.36	130	5.71	180	8.23	230	10.91	280	13.71
31	1.24	81	3.40	131	5.76	181	8.29	231	10.96	281	13.76
32	1.28	82	3.45	132	5.81	182	8.34	232	11.02	282	13.82
33	1.32	83	3.49	133	5.86	183	8.39	233	11.07	283	13.88
34	1.36	84	3.54	134	5.91	184	8.44	234	11.13	284	13.93
35	1.40	85	3.58	135	5.96	185	8.49	235	11.18	285	13.99
36	1.44	86	3.63	136	6.00	186	8.55	236	11.24	286	14.05
37	1.48	87	3.67	137	6.05	187	8.60	237	11.29	287	14.11
38	1.53	88	3.72	138	6.10	188	8.65	238	11.35	288	14.16
39	1.57	89	3.77	139	6.15	189	8.70	239	11.40	289	14.22
40	1.61	90	3.81	140	6.20	190	8.76	240	11.46	290	14.28
41	1.65	91	3.86	141	6.25	191	8.81	241	11.51	291	14.34
42	1.69	92	3.90	142	6.30	192	8.86	242	11.57	292	14.40
43	1.74	93	3.95	143	6.35	193	8.91	243	11.62	293	14.45
44	1.78	94	4.00	144	6.40	194	8.97	244	11.68	294	14.51
45	1.82	95	4.04	145	6.45	195	9.02	245	11.73	295	14.57
46	1.86	96	4.09	146	6.50	196	9.07	246	11.79	296	14.63
47	1.91	97	4.14	147	6.55	197	9.13	247	11.84	297	14.69
48	1.95	98	4.18	148	6.60	198	9.18	248	11.90	298	14.74
49	1.99	99	4.23	149	6.65	199	9.23	249	11.95	299	14.80
50	2.03	100	4.28	150	6.70	200	9.29	250	12.01	300	14.86
Millivolts per ° C.	0.041	Millivolts per ° C.	0.045	Millivolts per ° C.	0.048	Millivolts per ° C.	0.052	Millivolts per ° C.	0.054	Millivolts per ° C.	0.057

TABLE 25

Copper vs. Constantan Thermocouple

(Degrees centigrade; below ice point reference junction 0° C.)

° C.	Milli-volts	° C.	Milli-volts	° C.	Milli-volts	° C.	Milli-volts
−200	5.54	−150	4.60	−100	3.35	−50	1.81
199	5.52	149	4.58	99	3.32	49	1.77
198	5.51	148	4.56	98	3.29	48	1.74
197	5.49	147	4.54	97	3.27	47	1.71
196	5.48	146	4.51	96	3.24	46	1.67
195	5.46	145	4.49	95	3.21	45	1.64
194	5.44	144	4.47	94	3.18	44	1.60
193	5.43	143	4.45	93	3.15	43	1.57
192	5.41	142	4.42	92	3.12	42	1.54
191	5.40	141	4.40	91	3.09	41	1.50
190	5.38	140	4.38	90	3.06	40	1.47
189	5.36	139	4.35	89	3.03	39	1.43
188	5.34	138	4.33	88	3.01	38	1.40
187	5.33	137	4.31	87	2.98	37	1.36
186	5.31	136	4.28	86	2.95	36	1.33
185	5.29	135	4.26	85	2.92	35	1.29
184	5.28	134	4.23	84	2.89	34	1.26
183	5.26	133	4.21	83	2.86	33	1.22
182	5.24	132	4.19	82	2.83	32	1.19
181	5.22	131	4.16	81	2.80	31	1.15
180	5.20	130	4.14	80	2.77	30	1.11
179	5.19	129	4.11	79	2.74	29	1.08
178	5.17	128	4.09	78	2.70	28	1.04
177	5.15	127	4.06	77	2.67	27	1.01
176	5.13	126	4.04	76	2.64	26	0.97
175	5.11	125	4.01	75	2.61	25	0.93
174	5.09	124	3.99	74	2.58	24	0.90
173	5.07	123	3.96	73	2.55	23	0.86
172	5.05	122	3.94	72	2.52	22	0.83
171	5.04	121	3.91	71	2.49	21	0.79
170	5.02	120	3.89	70	2.46	20	0.75
169	5.00	119	3.86	69	2.43	19	0.72
168	4.98	118	3.83	68	2.39	18	0.68
167	4.96	117	3.81	67	2.36	17	0.64
166	4.94	116	3.78	66	2.33	16	0.60
165	4.92	115	3.76	65	2.30	15	0.57
164	4.90	114	3.73	64	2.27	14	0.53
163	4.88	113	3.70	63	2.23	13	0.49
162	4.86	112	3.68	62	2.20	12	0.46
161	4.84	111	3.65	61	2.17	11	0.42
160	4.82	110	3.62	60	2.14	10	0.38
159	4.79	109	3.60	59	2.10	9	0.34
158	4.77	108	3.57	58	2.07	8	0.31
157	4.75	107	3.54	57	2.04	7	0.27
156	4.73	106	3.52	56	2.01	6	0.23
155	4.71	105	3.49	55	1.97	5	0.19
154	4.69	104	3.46	54	1.94	4	0.15
153	4.67	103	3.43	53	1.91	3	0.12
152	4.65	102	3.41	52	1.87	2	0.08
151	4.62	101	3.38	51	1.84	1	0.04
150	4.60	100	3.35	50	1.81	0	0.00
Millivolts per ° C.	0.019	Millivolts per ° C.	0.025	Millivolts per ° C.	0.031	Millivolts per ° C.	0.036

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